RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor.....C. C. DAVIS
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Secretary-Treasurer.....H. E. SIMMONS

Vol. II July, 1929 No. 3

CONTENTS

General Subjects

		Page
Rubber Division Activities	H. E. SIMMONS	lvii
New Books and Other Publications		lx
A Survey of Recent Literature on the Chemistry of Rubber		lxiv

Reprinted Papers

The Oxidation of Vulcanized Rubber. By A. VAN ROSSEM and P. DEKKER	341
An Attempt at a Rational Classification of the Principal Accelerators of Vulcanization. By G. MARTIN and R. THIOLLET	356
Determination of the Iodine Number of Raw Rubber. By ADOLF GORGAS	362
Observations on the Chemical Constitution and Physical Properties of Rubber. By LOTHAR HOCK and GUIDO FROMANDI	365
The Purification and Fractionation of Rubber. By RUDOLF PUMMERER, ALBRECHT ANDRIESSEN and WOLFGANG GÜNDEL	367
The Preparation and Molecular Size of Isorubber Nitrone. By RUDOLF PUMMERER and WOLFGANG GÜNDEL	373
The "Freezing" of Raw Rubber. By A. VAN ROSSEM and J. LOTICHIUS	378
The Tackiness of Unvulcanized Rubber. By T. L. GARNER	384
The Absorption of Oxygen by Rubber. By G. T. KOHMAN	390
Some Practical Aspects of Rubber Evaluation. By R. P. DINSMORE	406
Pigment Reinforcement. By R. W. LUNN	409

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the Act of August 24, 1912.

The Nature of Vulcanization. Part IV. By H. P. Stevens and W. H. Stevens 421
Some Observations on Rubbers with Low Nitrogen Content. By A. D. Cummings and L. B. Sebrell 431
Natural and Synthetic Rubber. I—Products of the Destructive Distillation of Natural Rubber. By Thomas Midgley, Jr., and Albert L. Henne .. 441
Natural and Synthetic Rubber. II—Reduction of Isoprene by $Na-NH_3$. By Thomas Midgley, Jr., and Albert L. Henne 452
Natural and Synthetic Rubber. III—Dimethyloctadiene. By Thomas Midgley, Jr., and Albert L. Henne 450
Effect of Antioxidants in Typical Rubber Stocks. By Marion C. Reed ... 456
A Temperature-Recording Micropress for Studying the Course of Vulcanization. By James C. Walton 462
Chart for the Estimation of Equivalent Cures. By C. L. Brittain 471

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....ARNOLD H. SMITH, Rubber Service Laboratories
Vice Chairman.....STANLEY KRALL, Fisk Rubber Co.
Secretary-Treasurer.....H. E. SIMMONS, Municipal University, Akron
Executive Committee..H. L. FISHER, E. R. BRIDGWATER, S. M. CADWELL, C. W. SANDERSON, H. A. WINKELMANN

Minutes of the Meeting of the Rubber Division, Held in Columbus, Ohio, May 1, 1929

The meeting was held in the new Chemical Laboratory of the Ohio State University, with Stanley Krall, Vice Chairman of the Division in the chair, due to the absence of the Chairman, A. H. Smith, who at the present time is in Europe.

The attendance during the entire session of the Rubber Meeting was approximately two hundred-fifty.

Vice Chairman Krall appointed a Resolution Committee consisting of Harry L. Fisher, A. A. Somerville, and W. B. Wiegand.

The program was given as printed.

W. A. Gibbons gave a verbal report on the progress of the Physical Testing Committee during the past six months, which report showed that Mr. Rupert was engaged largely in the preparation of a report gathered from a questionnaire in regard to the methods employed in the physical testing of rubber in different laboratories.

The Secretary made a report showing at the time an active membership in the Division of 411 members, 185 Associate Members, 29 Honorary Members and 64 Subscribers.

The Secretary also called attention to the fact that approximately 200 of the members in 1928 had unpaid dues for the year 1929 and that 60 members had been dropped from the mailing list whose dues for 1928 had not been paid. Upon motion, duly made and seconded, the report was approved.

Under discussion of new business it was recommended that the Executive Committee make arrangements with the American Chemical Society whereby no formal program for the Rubber Division would appear in Minneapolis for the fall meeting, but instead a symposium be held in Akron or New York the latter part of September or the first of October.

The Treasurer made the following report, which by motion was made a matter of record:

Amount in the bank at the Swampscott Meeting.....	$1452.62	
Deposits (received in payment of dues).....	1462.00	$2914.62
Disbursements:		
Postage and telegrams.....	$18.11	
Translations.....	124.05	

Reprints and further expenses in printing RUBBER CHEM. & TECH.	284.25	
Mack Printing Company	580.22	
Letters and stationery	99.88	
Stenographic services	80.39	
Refunds	75.00	1261.90
Money in the bank April 30, 1929		$1652.72

The Resolution Committee made the following report which, upon motion, was made a part of the records of the meeting.

I. The Rubber Division sincerely expresses its cordial thanks to the following men comprising the local committee of the Division: A. C. Eide, M. K. Easley, and R. M. Reel for (1) the efficient aid given our members in obtaining hotel accommodations beforehand, (2) the help given in connection with the divisional meetings, and (3) the excellent arrangements for the Rubber Division Dinner and the entertainment accompanying it.

II. The Division also extends its cordial thanks to Professor William McPherson and the other members of his committee and student aides from the Columbus Section for this generous help in making this meeting such an outstanding success.

III. We recommend that the Secretary of the Division send greetings to our absent Chairman, Arnold H. Smith.

Respectfully submitted,

A. A. SOMERVILLE
W. B. WIEGAND
H. L. FISHER

Harry L. Fisher presented a communication from H. E. Howe which by correspondence had been agreed to between H. E. Howe and C. C. Davis to the following effect:

That in the future all papers presented before either the Rubber Division Meetings or Group Meetings that are rejected by H. E. Howe as not to be printed in INDUSTRIAL AND ENGINEERING CHEMISTRY, to be forwarded directly to C. C. Davis, who in conjunction with the authors will decide where best to submit the papers for publication.

By motion duly made and seconded this recommendation was approved.

By motion duly made and carried the office of Sergeant of Arms of the Division was created. The duty of said officer to notice whether or not people attending the Division meetings wear the official badge of registration and second to try and preserve order outside of the room in which the meeting is being held. It was suggested that the first Sergeant of Arms would be appointed by the Chairman of the Division.

A motion prevailed in which the creating of a Committee of three were instructed to draw up rules pertaining to the presentation of papers before the Division. The members of this committee are:

Upon motion duly made and seconded the meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

Group Meetings

The following local group meetings, not previously reported by the local secretaries, have been held in recent months:

Los Angeles Group

Oct. 16, 1928. Address by Charles R. Park on "Vulcanization."

Dec. 16, 1928. Address by W. R. Hucks on "Internal Mixers."

The following officers were elected: *Chairman*, A. F. Pond, Samson Tire & Rubber Co.; *Vice Chairman*, E. S. Pond, Golden State Rubber Mills; *Secretary-Treasurer*, T. Kirk Hill, Kirk Hill Rubber Co.

Jan. 31, 1929. Address by R. P. Dinsmore on "Some Practical Aspects of Rubber Evaluation."

March 29, 1929. Address by W. F. Zimmerli on "What Is Vulcanization of Rubber?"

Akron Group

Dec. 5, 1928. Addresses by Bradford Noyes on "Temperature Control in the Rubber Industry;" by R. W. Moorhouse on "The Temperature Control of Mill Rolls;" by Lawrence Keltner on "Calender Roll Temperatures;" and by C. B. Mitchella on "The Temperature Control of the Vulcanizer."

Jan. 28, 1929. General subject, "The Measurements of Rubber Thickness." Addresses by R. W. Brown on "Essentials for Accurate Gauging of Compressible Materials;" by E. O. Dieterich on "Some Practical Methods of Gauging Thickness at Calenders;" and by R. D. Evans on "Some Causes of Variability of Gauge and Unit Weight of Calendered Products."

The following officers were elected: *Chairman*, G. K. Hinshaw, Goodyear Tire & Rubber Co.; *Vice Chairman*, K. D. Smith, B. F. Goodrich Co.; *Secretary-Treasurer*, C. W. Sanderson, Goodyear Tire & Rubber Co.

New York Group

Oct. 10, 1928. Address by C. R. Boggs on the "Manufacture, Technology, and Testing of Rubber-Covered Insulated Wire."

Nov. 10, 1928. Addresses by Herbert Rogers on the purposes and activities of the Institution of the Rubber Industry of England, and by Philip Schidrowitz on "Rubber as a Substitute for Leather."

The following officers were elected: *Chairman*, W. B. Wiegand; *Secretary Treasurer*, W. H. Cope.

March 20, 1929. General subject, "Stearic Acid for Rubber Compounding." Addresses by W. F. Russell on "The Early History of Stearic Acid Compounding;" by D. F. Cranor on "The Manufacture and Production of Stearic Acid;" by J. T. Blake on "Theoretical Aspects of the Wetting Action of Stearic Acid;" by H. A. Winkelmann on "The Use of Stearic Acid in Reclaimed Rubber;" by E. W. Fuller on "The Effect of Stearic Acid on Crude Rubber;" by J. R. Sheppard on "The Effect of Stearic Acid with Litharge;" by R. P. Dinsmore on "The Effect of Stearic Acid on Organic Accelerators;" and by C. O. North on "The Relation of Stearic Acid Content to Abrasive Index."

Boston Group

November 7, 1928. Address by Philip Schidrowitz on "Vulcanized Latex."

The following officers were elected: *Chairman*, J. M. Bierer, Boston Woven Hose & Rubber Co.; *Secretary-Treasurer*, T. M. Knowland, Hood Rubber Co.

New Books and Other Publications

1929 Yearbook. 93 pages. Tire and Rim Association, Inc., Cleveland, O.

In addition to full statistics on the number of rims of every type inspected and approved by the Association from 1917 to 1928, this annual contains complete load and inflation tables, diagrams of rim contours, a summary of the rim equipment of all American cars, and valve descriptions and drawings. The roster of the Association membership and the constitution and by-laws are also included. The 1929 Yearbook is printed in a larger size than in previous years, handsomely bound and thumb-indexed. [From *The Rubber Age.*]

Fifteenth Annual Report. 32 pages. International Association for Rubber and Other Cultivations in The Netherlands. The Hague, **1929.**

Detailed statistics on the production of plantation rubber in the Dutch East Indies are contained in this report, together with a summary of local labor problems, taxation, rubber thefts, and association activities. At the end of 1928 this association had 200 company members and 65 individual members. Appended to its own report, which is printed in both Dutch and English, is a separate 16-page report of its propaganda department, describing the work of that group in developing the applications of latex and the use of rubber flooring and rubber roadways. [From *The Rubber Age.*]

Gummi-Kalender 1929. Jahrbuch der Kautschuk-Industrie. Ein Hilfsbuch für Kaufleute, Techniker, Handler und Reisende der Kautschuk-, Asb est- und Celluloid-Branche. Edited by Ernst A. Hauser and Kurt Maier. Published by Union Deutsche Verlagsgesellschaft, Zweigniederlassung, Berlin. Cloth, $3^7/_8$ by $5^7/_8$ inches, 456 pages.

This little year book, as is known, is intended to be an aid to merchants, technicians, dealers, and salesmen of the rubber, asbestos, and celluloid industries. The 1929 issue, which has just appeared, while retaining the main features of its predecessors, has been carefully revised and amplified to bring it up-to-date. Thus in the technical section, a short article on the uses and treatment of latex has been added. Also various conversion tables and a table of atomic weights have been included, while in addition the method of calculating belting drives has been explained and the chief regulations affecting the manufacture of rubber and celluloid goods have been summarized. Latest business reports of some of the leading German rubber and asbestos firms again find a place, besides a variety of information calculated to assist the rubber man. [From *India Rubber World.*]

Encyclopedie du Caoutchouc et des Industries qui s'y Rattachent. Edited by the Syndicat deu Caoutchouc et des Industries qui s'y Rattachent. Published by *La Revue Générale du Caoutchouc*, 18 Rue Duphot, Paris, **1929.** Stiff covers, 500 pages, $7^1/_4$ by $10^3/_4$ inches, tables, graphs, illustrations.

Not since 1896 has a really comprehensive work on the rubber industry been published in France. To be sure, various useful manuals have recently appeared, but the need was felt by the Association of Rubber and Allied Industries for a work that would gather together the sum total of present knowledge on rubber. With this in view, coöperation of the best qualified French experts was secured, with what good results the present imposing volume bears ample testimony.

The four parts into which the subject matter has been divided cover the production of crude rubber, vulcanized rubber, the various manufactures, and scientific and technical research. Under the guidance of such men as Girard, Hauser, Bary,

Sloim, Boiry, Macré, Gazel, Audy, Bregeat, to name some of the contributors, the reader learns about crude rubber, reclaims, fillers, pigments, accelerators, antioxidants, and is finally initiated into the processes of producing a number of rubber articles. The part devoted to manufacture closes with a chapter on different methods and appliances for the recovery of solvents, also dipping equipment.

As to the volume itself, it is handsomely gotten up and well illustrated by a number of photographs. [From *India Rubber World.*]

Rubber. A current practical study of rubber and allied industries issued by Henderson Rubber Reports, Inc., 44 Beaver St., New York, N. Y. This illustrated folder is descriptive of a new loose leaf rubber statistical service of text and charts to be inaugurated with the new year, 1929. This service planned to be complete, concise, accurate, and pertinent, will present weekly, monthly, quarterly and yearly basic, current, and record charts on crude rubber, cotton, reclaim, stocks, and consumption. The service is introduced by a general manual of price factors and market practices of the rubber industry designed as a practical introduction to and reference handbook for the interpretation of the past and current activities of the rubber market. [From *India Rubber World.*]

Crude Rubber. Under this title H. Hentz & Co., Hanover Square, New York, N. Y., have issued a compilation of statistics on crude rubber, production, consumption, and prices, automobile production, U. S. consumption of gasoline. Figures are also given from consular reports showing monthly tonnage of rubber invoiced to the United States during 1928. Plantation rubber areas are tabulated for 1904 to 1927 together with maps indicating where rubber is grown. [From *India Rubber World.*]

The Realm of Rubber, being a record of existing conditions in the rubber industry. H. H. Ghosh. J. B. Daymond, 76 Dhurrumtollah St., Calcutta, **1928.** Cloth, 266 pages, $6^1/_2$ by 9 inches, charts add illustrations. Indexed.

This volume affords its readers a concise, systematic account of crude rubber cultivation, its origin, development, and present condition. Although written largely from the plantation point of view, it acquaints the rubber goods manufacturer with the important developments that affect the sources of his rubber supply.

The first ten chapters of the book cover the genesis of rubber culture and the essentials of its prosecution, the world's rubber sources and wild rubber in Brazil. Rubber production in India, Burma, and Ceylon is discussed, followed by two chapters on diseases and pests of Hevea.

The two closing chapters are devoted to synthetic rubber, the rubber market, and statistics on crude rubber. [From *India Rubber World.*]

La Gomme de Balata. A. D. Luttringer. A. D. Cillard, Paris. 49 pages. Paper $5^5/_8$ by $8^3/_4$ inches.

This is a volume of the encyclopedia of caoutchouc and of plastic substances. Balata gum has numerous industrial uses, but up to the present there is no work in existence devoted to this interesting material. The booklet covers the following subjects: General, Origin, Collection, Orinoco Valley, British Guiana, French Guiana, Surinam, Brazil, Peru, Properties, Washing, Applications, Use in Rubber Articles, Regeneration, Analysis, Price, World Production. [From *India Rubber World.*]

The Preparation of Plantation Rubber. Sidney Morgan, A.R.C.S., visiting agent and technical adviser for Estates in the East, formerly chief scientific officer of the Rubber Growers' Association. Preface and a chapter on vulcanization by Henry P. Stevens, consulting chemist to the Rubber Growers' Association in

London. Second Edition. Constable & Co., Ltd., 10–12 Orange St., London, W. C. 2, England. Red Cloth, 357 pages. Illustrated and indexed. 6 by 9 inches.

This book may well be called the Bible of the rubber planting industry, and in its new revised edition it is indispensable, more so than ever before, to those interested in rubber. The book is divided into six parts, covering adequately the topics of field operations, factory operations, machinery and buildings, the finished rubber, general items, and vulcanization. It is well indexed and profusely illustrated.

Some idea of the value and scope of the book may be realized from the following excerpt from the preface to the first edition:

"An earlier book, published in 1913, by the Rubber Growers' Association, entitled 'The Preparation of Plantation Rubber,' was well received and widely read. The book dealt in a very practical manner with problems with which the industry had to contend. A second edition was subsequently published. Both editions are now out of print. The present opportunity was therefore taken to revise the original work, with the result that it has been enlarged and practically rewritten. The information given is brought up to date, and covers the whole process of production commencing with the planting of the tree, passing on to the collection, coagulation, and curing of the rubber, and concluding with the packing for export. In the course of his work for the Association, Mr. Morgan carried out a great deal of industrial research in rubber production, including lengthy experiments on tapping, the use of different coagulants and different conditions of coagulation, and also on varying modes of rolling, drying, and smoking rubber. He also went very fully into the types of construction and details of the machinery and buildings employed on the estates." [From *India Rubber World.*]

Investigations of the Imperial Institute on Samples of Plantation Para Rubber from Ceylon. Bulletin No. 49. Colombo, Ceylon, H. Ross Cottle, Government Printer, **1928.**

This pamphlet of 9 pages is a report on the "Causes of Variation in Plasticity," prepared in connection with the rubber research scheme at Peradeniya, Ceylon. In connection with the experiments reported it is pointed out that none of the methods employed in the determination of plasticity gives results which bear a known relation to a strictly defined physical property. [From *India Rubber World.*]

American Railway Association Specifications for Mechanical Rubber Goods. A 40-page pamphlet issued by The Rubber Association of America, Inc., New York, N. Y.

The booklet sets forth "Standard" and "Recommended Practice" specifications for various types of rubber hose commonly used by railroads, including "General Instructions on Standard Methods of Tests for Mechanical Rubber Goods."

Prior to 1923, every railroad had separate and distinct specifications for hose, and to avoid waste and confusion resulting from this condition, the Committee on Specifications and Tests for Materials—Mechanical Division of the American Railway Association, and the Specification Committee—Mechanical Rubber Goods Manufacturers division of the Rubber Association, joined in formulating A. R. A. "Standard" and "Recommended Practice" specifications.

For the last five years the Mechanical Goods Division of the Rubber Association has urged the adoption of these A. R. A. specifications, as they have been revised from time to time, by individual railroads buying rubber goods according to detail specifications. Today it is estimated that 90 per cent of the railroad hose bought under detail specifications is purchased according to these specifications. Copies of the booklet are available upon application to the Rubber Association of America. [From *India Rubber World.*]

British Standard Specification for Friction Surface Rubber Transmission Belting. The British Engineering Standards Association, 28 Victoria St., London, S. W. 1. Paper; 11 pp., $5^1/_2$ by $8^1/_2$ inches. Illustrated.

This pamphlet, No. 351, issued February, 1929, covers the standard practice with regard to the specifications and testing of friction surface belting. The term "friction surface" is defined and the specifications prescribe construction, materials, and dimensions. Methods of testing and service conditions are detailed. [From *India Rubber World.*]

Tractive Resistance of Automobile and Coefficients of Friction of Pneumatic Tires. T. R. Agg. Engineering Experiment Station, Iowa State College, Ames, Iowa. Paper, 60 pages, 6 by 9 inches. Illustrations and graphs.

This is a report of a highway investigation conducted by the Iowa Engineering Experiment Station in coöperation with the United States Bureau of Public Roads. A summary of the more significant results of the investigation of tractive resistance is given. [From *India Rubber World.*]

Rubber Producing Companies with List of Directors and Secretaries. Compiled by the Mincing Lane Tea & Rubber Share Broker's Association, Ltd. London, Nov., **1928.**

This annual reference publication contains a brief review of the development of the crude rubber producing industry for the past few years with tabulations of the planted areas of the principal countries, their present and future potential output. The data listed for the several hundred tea and rubber plantations include their directors, executives, capital, production, etc. The volume forms a reliable directory for commercial reference. [From *India Rubber World.*]

Le Recaoutchouteur Francais is a new French trade journal issued bimonthly in the interests of the French retreading industry. It is the official organ of the Syndicate General des Patrons Recaoutchouteurs de France at des Colonies (General Association of the Retreaders of France and the Colonies) now being formed. The editor and founder is Leon Eglene, the editorial offices at Rue du Sport, Vichy (Allier). [From *India Rubber World.*]

La Goma is a new magazine published monthly in Barcelona, Spain, for the rubber industry. The periodical deals with gutta percha, insulated wire, ebonite, celluloid, and other plastic materials, and also their derivatives and applications. Juan Blanch Guerrero is editor and publisher. [From *India Rubber World.*]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the April 10 and 20, May 10 and 20, and June 10, 1929, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Modern rubber research laboratory. ANON. *India Rubber World* **79**, No. 3, 65–6 (1928).—An illustrated description of the labs. of the N. J. Zinc Co. at Palmerton, Pa. C. C. DAVIS

Manufacturing rubber goods from latex by electrodeposition. PAUL KLEIN. Hungarian Rubber Works, Budapest. *Rubber Age* (N. Y.) **24**, 319–21(1928).—See *C. A.* **22**, 4877; **23**, 1305. C. C. DAVIS

Determination of the rubber content in latex preserved with trisodium phosphate and formalin. W. SPOON AND N. BEUMÉ-NIEUWLAND. *Arch. Rubbercultuur* **12**, 659–71(1928). (Summarized in English 672–4).—In developing a method for detg. the rubber latex preserved with 0.2% Na_3PO_4 and 0.2% HCHO, the influence of various factors had to be ascertained. *Weighing the latex.*—The most satisfactory way was to weigh 200 g., since adding latex drop by drop at the end requires no more time than weighing an arbitrary portion. *Coagulation with acid of various concns.*—As with fresh latex and latex preserved with NH_3, the yields of rubber from latex preserved with Na_3PO_4 + HCHO increased with increase in the concn. of acid. Much smaller increases occurred when the quantity of acid was increased. As a standard for coagulation, 15 cc. of 10% AcOH per 100 cc. of latex was adopted. *Age of latex.*—With the foregoing quantity and concn. of AcOH, coagulation was complete regardless of the time of standing previously. *Comparison of latex contg. NH_3 and that contg. Na_3PO_4 + HCHO.*—With the foregoing quantity and concn. of AcOH, the results were exactly the same as with latex contg. NH_3 dild. with an equal vol. of water and treated with 25 cc. of 20% AcOH (per 100 cc. of original latex). *Addn. of a fixed or variable quantity of acid.*—Addn. of 10% acid until thickening begins while stirring leads to variable results. *Influence of the quantity of HCHO.*—Excess inhibits coagulation, AcOH thickening the latex but failing to produce a coherent clot. When the HCHO eventually evaps., a clot usually forms. *Influence of time between coagulation and milling.*—With increase in the time from coagulation to milling, the wt. increases. *Influence of drying.*—Prolonged drying *in vacuo* has no effect on the final wt. *Procedure for the detn.*—Shake the sample, thoroughly weigh exactly 200 g. in an Al bowl, add 300 cc. of 10% AcOH or 5% HCO_2H with continuous stirring, cover and let stand 2–3 hrs., knead and crepe the coagulum under standardized conditions, dry in the air overnight, roll in paper, dry *in vacuo* for 2 hrs., place in a desiccator over CaO and weigh the next day (to centigrams). C. C. DAVIS

Coagulation phenomena in Hevea latex. VIII. Rubber obtained by freezing the latex. O. DE VRIES AND N. BEUMÈ-NIEUWLAND. Proefstation voor Rubber, Buitzorg (Java). *Arch. Rubbercultuur* **12**, 675–82(1928). (Summarized in English 683–5); (cf. *C. A.* **23**, 304).—Coagulation takes place only considerably below 0°. Even at —15° coagulation is complete only after about 5 days. The coagulum obtained by freezing has a peculiar structure. The surface layer is a coherent film as in ordinary coagulation, but beneath it is a network of thick and thin white threads with ice crystals between. When sufficiently cold, the mass is hard and brittle, but when the ice melts the threads of rubber bind together to form a coherent coagulum from which clear serum is exuded. The properties of this coagulum do not differ from those of ordinary coagulum except that it is yellower. The serum is a clear yellow color, with a p_H value of 6.2. Boiling does not form a ppt., but on addn. of a trace of AcOH and further boiling a ppt. appears. Addn. of 2.5% AcOH to the serum forms a flocculent ppt., which

gives the biuret and Millon reactions for proteins. The serum also forms ppts. with NaCl, $MgSO_4$ and $(NH_4)_2SO_4$ solns., and with dil. alkali a ppt. which redissolves in excess. The serum coalesces B-mixt., whereas the ppt. obtained by acidifying the serum has no coalescing power. Furthermore, in ordinary coagulation this coalescing agent is adsorbed by the coagulum (cf. *C. A.* **19**, 419; **22**, 698). The following data give the analytical results on coagula obtained by coagulation by AcOH and by freezing, resp.: % ash, 0.22, 0.23; % acetone ext., 3.3, 3.3; % N, 0.39, 0.31; viscosity, 31, 33; viscosity (after acidification), 16, 17; plasticity (d_{30}), 1.47, 1.54; tensile strength, 1.46, 1.51; time of cure, 108, 100; slope, 36, 35.5. The % N shows that with frozen rubber a considerable part of the proteins remain in the serum. Nevertheless, rubber from frozen latex vulcanizes more rapidly than that from acid coagulation. Prolonged freezing of latex does not materially affect the plasticity. Even after being frozen 7 months, the plasticity changes but little, while the viscosity remains the same. C. C. D.

The determination of inorganic matter in soft rubber goods. S. Minatoya, H. Okuhara and S. Ohki. *Res. Electrotech. Lab.* (Japan) No. **234**, 42 pp.(1928). (In Japanese, with synopsis in English.)—The method uses solid paraffin as a disintegrating agent. Heat 1 g. of finely divided sample with 10 g. of paraffin at 180° until completely dispersed and the mineral substances are settled out, while still warm add 70 cc. of petroleum benzine, keep warm for 15 mins., centrifuge (2500 r. p. m.), decant, add fresh benzine, centrifuge again, decant, add to the residue a mixt. of acetone and $CHCl_3$ (equal wts.), boil, decant or siphon, repeat 3 times, dry and weigh. The acetone-$CHCl_3$ is particularly effective in removing decompn. products of rubber, and there is no fear of high results. C. C. Davis

The solubility of sulfur in rubber. Heinrich Loewen. *Kautschuk* **4**, 243–9 (1928).—A review and discussion of the literature, with photomicrographs of *droplets of supercooled S in rubber, rhombic crystals of S in rubber, monoclinic crystals of S in rubber accompanied and unaccompanied by droplets of S*, the *boundary between rhombic and monoclinic crystals* both newly formed and after 7 hrs., *sepn. of S induced by light* both newly formed and after 7 yrs., and the *diffusion of S into the interior of rubber during vulcanization* in a S bath. A gradual disappearance of cryst. S in the micro-sections during the years is ascribed to "after-vulcanization," which consumes part of the S in soln. and therefore allows some of the crystd. S to pass into soln. All evidence points to the fact that S dissolves in the mol. state in rubber, the *mol.* probably being S_8. There is no evidence of the existence of "thiozone" or "thiozonides." When a rubber-S mixt. is alternately heated and cooled above and below the m. p. range of S, there is no sharply defined "soln. point," but rather an interval. Soln. of the rubber-S mixt. in C_6H_6, with subsequent evapn. of the solvent, allows the prepn. of mixts. particularly suitable for such a study. When a rubber-S mixt. is heated to 120° to fuse the S and dissolve it, and is then cooled, droplets of S appear at a certain temp. range (depending upon the proportion of S) and the mixt. becomes microscopically turbid. Because of supercooling, this temp. does not coincide exactly with the soly. of S, but is lower. If the mixt. is then warmed slowly, it again becomes clear, but not uniformly, some portions remaining turbid longer than others. There is accordingly no sharp "soln. point," but only an interval. The same phenomenon is evident when the rubber-S mixt. is dissolved in C_6H_6 and the latter is then evapd. at 60–80°, the resulting clear mixt. being particularly suitable for quant. measurements of the *soly. of S in unvulcanized rubber*. Through observations of the temp. at which turbidity appears on cooling, and the temp. at which the mixt. becomes clear on heating, the *soly. of liquid S in unvulcanized rubber* was found to be 5% at 53°; 7.5% at 86–7° and 10% around 108°. C. C. Davis

The photometric determination of the blackness of various types of carbon black. Lothar Hock. Univ. Giessen. *Kautschuk* **4**, 266–8(1928).—With the photometric method for detg. blackness which is described, it was found that there is a close relationship between the sp. surface, *i. e.*, the surface of a definite wt. of C black, and the blackness of the latter, the greater the sp. surface the more intense the blackness. Accordingly, the quality of a C black may in an approx. way be judged by its blackness. The sp. surfaces were measured indirectly by detg. the heats of wetting (cf. H. and Bostroem, *C. A.* **21**, 1335; Bostroem, *C. A.* **22**, 4271). A series of blacks was chosen with heats of wetting ranging from 0.45 to 5.23 Cals., *i. e.*, from a gray colored one to an intense black one. The blacks were then mixed (1) with 100 parts of lithopone and (2) into rubber-ZnO mixts., and each mixt. was compared with pure lithopone or with rubber-ZnO by measuring the relative intensities of reflection of light by means of a Marten polarization photometer for measuring blackness (cf. Weigert, *Optische Methoden der Chemie*, *C. A.* **22**, 536), or better by means of a recently developed leucometer (manufactured by Schmidt and Haensch as a modification of the unimeter of Bloch, *C. A.* 22, 3069). The following data give the heats of wetting (g.-Cals.), photometric angles

for the lithopone mixts., leucometric reflections (as % of the reflection of pure lithopone) and the leucometric reflections (as % of the reflection of rubber-ZnO), resp., for 6 blacks: (1) 0.45, 35.6, 50.5, 9.3; (2) 1.32, 31.9, 39.0, 4.2; (3) 2.71, 26.2, 24.1, 2.1; (4) 2.86, 26.5, 24.8, 2.0; (5) 4.08, 28.1, 28.5, 2.0; (6) 5.23, 25.5, 22.7, 2.5. The method is also applicable to the quant. measurement of the color imparted by other pigments to rubber mixts. C. C. DAVIS

The evaluation of carbon blacks. D. F. CRANOR AND H. A. BRAENDLE. Binney & Smith Co., New York City. *India Rubber World* **79,** No. 4, 67–8(1929).—The conclusions are based on exptl. data, rubber-S-PbO-C black mixts. being used, because with such mixts. the rate of vulcanization is not greatly influenced by the C blacks. The blacks tested included a reënforcing black of standard quality, a moderately reënforcing high yield black, a soft high yield black, and 2 exptl. blacks. The ΔA values (energy capacities) were 100, 64, 35, 64, and 21, resp. In general the results show that the ΔA function as defined by Wiegand (cf. *C. A.* **19,** 3386) can be utilized to judge the relative merits of C blacks in practical rubber compounding. It will indicate not only the quality at the optimum concn. of C black but also the range of concn. over which the C black is effective. When C blacks of similar type are concerned, it is important to supplement the information gained from the ΔA function by other stress-strain data and by performance tests in the lab. and in service. C. C. DAVIS

An improved oxygen bomb. ANON. *India Rubber World* **79,** No. 5, 75–6(1929).—A new type of O-bomb and accessories (cf. Bierer and Davis, *C. A.* **18,** 2617; **19,** 3172), which has been designed at Du Pont de Nemours & Co., is described and illustrated. A battery of bombs is heated in a water bath. Each bomb has a Ni safety disk for a max. of 475 lb. per sq. in. pressure, and a thermometer well to detect differences between the internal temp. and that of the water. The water is heated in a const.-temp. tank by steam coils, with control of temp. at 70° ± 0.5°, and is circulated through the bath. Various other features are described, including the method of charging and discharging O. A max. of 8% of the internal capacity of a bomb should be occupied by rubber samples. C. C. DAVIS

Note on the evaluation of antioxidants. T. L. GARNER. *India Rubber J.* **77,** 31 (1929); cf. *C. A.* **22,** 3804.—When an antioxidant is tested in an unaccelerated mixt. the time of vulcanization must often be adjusted to counteract the accelerating or retarding effect of the antioxidant, and it is much better to use an accelerated mixt., where the effect of the antioxidant is masked by sufficient acceleration by an accelerator. Expts. with various mixts. led to the adoption of the mixt.: rubber 100, S 3.5, diphenylguanidine 1, ZnO 3, antioxidant 0.5–1, as a *standard for testing antioxidants.* The antioxidant properties of the various substances were judged by the aging of the mixts. in the Geer oven at 70°. In the mixt. above, the order of merit of various antioxidants depended upon the state of cure of the mixts., an antioxidant which gave the best protection in badly overcured mixts. not giving the best results in normally cured mixts. In general the beneficial effect of antioxidants was relatively great in overcured mixts. Only 1 among 9 antioxidants failed to discolor a white mixt., and most of them showed a tendency to stain, bad stains being made on wood pulp. The colors imparted by antioxidants to white mixts. vary greatly in ultra-violet light, and these colors change gradually on continued exposure, so that the color combinations on immediate and prolonged exposure offer a means for the *identification of individual antioxidants.* C. C. D.

The stickiness of unvulcanized rubber. R. W. GRIFFITHS AND MALDWYN JONES. *Trans. Inst. Rubber Industry* **4,** 235–46(1928).—The great importance in present mfg. processes of the property of stickiness in vulcanized rubber mixts. suggested the need of a *quant. method* of testing this property. In the test which has been developed by G. and J., the force required to sep. 2 surfaces which have been in contact under a definite load for a definite time is measured. With the *app.* which is described and illustrated, the adhesion between rubber sheets and their linings can be measured at different temps. By this means it was shown that stickiness increases with the time of mastication, and that under the same condition of mastication, washed rubber is less sticky than unwashed rubber. The tackiness of calendered sheets depends upon the temp. of the calender, speed of calender, and subsequent cooling before entering the lining. Mixts. apparently unsatisfactory can be rendered usable by regulating the calendering conditions. Sudden chilling, *e. g.*, by a cold bottom roll, destroys the desired tackiness by inducing a S bloom. The new app. will reveal differences in tackiness between the 2 sides of a calendered sheet. When a calendered mixt. is wrapped in lining, its stickiness several days later is distinctly higher than the stickiness of the same sheet left exposed to the air. The results show the need of cooling processed mixts. under controlled conditions before they enter linings, *e. g.*, by air jets or atomized water sprays. To prevent blooming, it is necessary at times to graduate the temp. of the cooling drums in such a way that

the hot fabric does not first come in contact with too cool a drum. A general discussion follows. C. C. DAVIS

A new physical test for vulcanized rubber. D. D. WRIGHT. Hood Rubber Co., Watertown, Mass. *Ind. Eng. Chem., Analytical Ed.* **1**, 17–20(1929).—Vulcanized rubber must often withstand torsion, tearing, and bending as well as compression, stress, and shear, and, furthermore, on aging the resistance to tearing and shearing often diminishes faster than does the resistance to simple stress. These facts were sufficient to warrant the development of a new test, in which a new design of test sample permits subjecting the sample to a combination of tensile and shearing stresses, which shear the predominant stress. This new *"tongue shear" test*, so named from the shape of the test piece, is described in detail and illustrated. It is of special value (1) in revealing "shortness," inner tubes being found to deteriorate relatively sooner as judged by this test than by tensile strength or stress-strain curve measurements; (2) as an unusually sensitive means of detecting the deterioration which takes place during artificial aging and (3) in detecting the beginning of overcuring, the test indicating poor resistance to sudden stress, low resistance to shear and exceedingly poor tearing quality in tubes which judged by tensile strength tests may appear to be of satisfactory quality. C. C. DAVIS

Effect of temperature on the stress-strain properties of vulcanized rubber. A. A. SOMERVILLE AND W. H. COPE. R. T. Vanderbilt Co., New York City. *Trans. Inst. Rubber Industry* **4**, 263–86(1928).—To ascertain to what extent in general the quality of rubber products depends upon their temp., the following relations were studied: (1) differences in the stress-strain curves of a typical tire at different temps. from 0° to 100°; (2) differences in the stress at different elongations at different temps. from 0° to 100°; (3) differences in the stress-strain curves of different cured rubbers; (4) the effect of the time of cure and the effect of overcure on the stress-strain curves at different temps.; (5) the effect of the % S and the % accelerator on the stress-strain curves at different temps.; (6) the effect of antioxidants on the stress-strain curves at different temps.; (7) the effect of fatigue on the stress-strain curves at 0° and 100°; (8) the effect of the permanent set at 0° and 100°; and (9) differences in stripping tests at 0° and 100°. For app., an ordinary testing machine, was equipped with a glass-windowed chamber contg. water at the required temp., through which the sample was stretched. With increase in temp. the stress-strain curves of the tire tread (rubber-S-accelerator-antioxidant-softener-ZnO-C black) approached the elongation axis, *i. e.*, for a given elongation the stress became progressively smaller with increase of temp. The difference between 0° and 100° was very great, at 400% elongation the stresses being approx. 2700 and 600 lbs. per sq. in., resp. The relative changes at different elongations were not const., the higher the elongation the greater being the proportional decrease in stress for a given increase in temp. The effect of an increase in temp. on the stress-strain curve differed for different rubbers, *e. g.*, guayule mixts. showing greater changes than fine para, smoked sheet, or crepe mixts. The state of cure of a mixt. had a great influence on the changes in its stress-strain curves with changes of temp., the stresses at 400% elongation both at 0° and at 100° increasing with increase in the time of cure. In tests where the % S was varied over a wide range, the min. difference between the stress-strain curves at 0° and 100° occurred with 2–3% S (based on the rubber). Hence for the ordinary type of rubber mixt. which must withstand elevated temps., 2–3% S is the best proportion to use for curing. At the optimum cure, the proportion of accelerator had less influence on the sensitivity of the stress-strain curves to temp. than did the S. However, with high acceleration, a reduction of S from 4 to 2% diminished the sensitivity of the stress-strain curves to temp. When samples were repeatedly elongated 400% and immediately released, the stress-strain curves both at 0° and 100° approached a const. position which differed greatly from the initial curve. When the samples were stretched in a similar way but were held 5 min. each time before release, there was a still greater difference between the initial and final curves, both at 0° and at 100°. In stripping tests of rubberized fabric belting at 0°, 25° and 100°, the friction stress at 100° was about 0.5 that at 0°. In an overcured mixt., the stress-strain curve at 0° may not reveal an overcure, and yet the curve at 100° may show an exceedingly "short" condition. Some mixts. have a much wider range than others over which they may be cured without suffering an overcure, but an overcured state can always be detected at 100° with a readiness which has not been possible with any previous test. It is, therefore, very important not to overcure products which must withstand elevated temps. Tests at 0° and at 100° of mixts., with and without antioxidants, in different states of cure, and which had been aged in air at 70°, showed that deterioration is not in this case a result of overcuring, for the stress-strain curves both at 0° and 100° changed in the same general manner. In this test, the longer the cure,

the faster the rate of deterioration. Addn. of an antioxidant retarded the rate of deterioration, particularly with overcured mixts., but it did not alter the relations between the stress-strain curves at 0° and 100°. In conjunction with earlier expts. by van Rossem and van der Meijden (*C. A.* **22**, 1059) and others, the results show how much poorer in quality rubber mixts. are when hot than when cold, particularly when they are overcured. Also in *India Rubber World* **79**, 64–71(1928) and *Rubber Chemistry and Technology* **2**, 1–20(1929). C. C. DAVIS

Some new laboratory work on rubber. A. A. SOMERVILLE AND J. M. BALL. R. T. Vanderbilt Co., New York City. *Rubber Age* (N. Y.) **24**, 490–4(1929).—With most rubber mixts. there is a wide difference between the stress-strain curves at 0° and at 100°, the mixts. becoming relatively weak, particularly when overcured (cf. preceding abstr.). There are, however, 3 types of mixts., the stress-strain curves of which at 0° and at 100° cross in such a way that at low elongations the stresses at 100° are higher than those at 0°, while at higher elongations (up to the breaking point) the stresses at 100° are lower than those at 0°, *viz.*, rubber cured with (1) 1–1.5% S and a high % of accelerator; (2) tetramethylthiuramdisulfide and neither S nor other accelerator, and (3) a low % of S, an org. accelerator and Se. With this 3rd type of mixt., the elongation at which the stress-strain curves cross depends not only upon the ingredients and their proportions but also upon the state of cure, the higher the latter the higher the crit. elongation. Stripping tests of rubberized fabric belts show strikingly the effects of overcure, for at 0° the "friction" values of belts correctly cured and overcured may be virtually the same, and yet at 100° the friction of the overcured belts may be perhaps only 0.5 that of the correctly cured belts. Furthermore, such belts show just as strikingly the *effect of Se*, for, where without Se the friction values diminish progressively with increase of temp., addn. of Se results in progressive increases of friction strengths with increase of temp., so that the values are not only higher at room temp. but become proportionately still higher at 100°. The results are obtained with Se when the belts are judged by means of flexing tests. The use of Se in mixts. used in the construction of automobile fan belts has proved to be of great value in lengthening the span of life of the belts. **Discussion.** J. M. BIERER. *Ibid* 493.—Replacement of part of the S by Se in a belt friction mixt. resulted in twice the resistance to flexing. EVERETT MORSS. *Ibid* 493–4.—A brief history of the development of the use of Se by Boggs is given (cf. B. and Follansbee, *C. A.* **21**, 1566). GLIDDEN. *Ibid* 494.—Replacement of part of the S by Se in a tire-tread mixt. shortened the time of optimum cure, increased the tensile strength and hardness and slightly improved the aging. SCHILDHAUER. *Ibid* 494.—Replacement of part of the S by Se in belt friction mixts. resulted in increases of flexing tests from 30,000–85,000 to 150,000–200,000 cycles. JOHN T. BLAKE. *Ibid* 494.—The expts. of Somerville (*loc. cit.*) suggest that Se increases the range of cure over which a mixt. does not overcure. At ordinary vulcanizing temps. about 0.5% Se dissolves in rubber, but no reaction takes place (even up to and above the m. p. of Se) unless an accelerator is added. The soly. explains, however, why Se is active as a vulcanizing agent far below its m. p. All attempts to make hard rubber with Se alone have failed. Soft rubber and hard rubber are different substances. Hard rubber is a plastic which is sensitive to temp. changes, whereas true soft rubber is elastic and is relatively insensitive to temp. changes, so that when rubber is cured with Se and insufficient S to endanger overcuring, the resulting vulcanizate is relatively insensitive to temp. changes. A. A. SOMERVILLE. *Ibid* 494.—Results indicate that when a mixt. contains not over 2% S (based on the rubber) and not over 1% Se, there is little or no tendency to bloom. C. C. DAVIS

Synthetic rubber from coal. FRITZ HOFMANN. *Rubber Age* (N. Y.) **24**, 322–3 (1928).—An address, dealing with past work. C. C. DAVIS

Rubber solvent gasoline. BRUCE C. DODD. Anderson-Prichard Oil Corp., Oklahoma City. *India Rubber World* **79**, No. 3, 68(1928).—A brief review of the development of gasoline solvents for use in the rubber industry, with a description of the com. solvents termed "Rub-Sol" and "Dip-Sol." These have distn. ranges of 40–145° and 98–145° resp., but give cements which dry in about the same length of time. The latter is particularly useful for dipped goods. C. C. DAVIS

Complete recovery of scrap rubber. E. ROUXEVILLE. *Rev. gén. caoutchouc* **6**, No. 48, 15–6(1929).—On the assumption that vulcanized rubber is not plastic because the viscous phase of raw rubber has been modified by S, it should be possible to reclaim vulcanized rubber by restoring to it a viscous phase and as a result its plasticity. Terebenthene may be polymerized by catalysts with the formation of a viscous *terpene* of the compn. $(C_{10}H_{16})n$, the phys. and chem. properties of which are similar to those of the viscous phase of raw rubber. It dissolves raw and vulcanized rubber, it vulcanizes in a mixt. with raw rubber and it does not influence the quality. Scrap rubber is finely

ground, mixed with 5–10% of the polymerized terpene, the ordinary proportion of S is added and the mixt. is vulcanized in the ordinary way. The polymerized terpene has an antioxidant effect. Because of its consistency it is better than rubber for impregnating cotton, jute, cork, etc. Various other applications are suggested.
C. C. DAVIS

Band tires. T. S. GARDNER. Dunlop Rubber Co. *Trans. Inst. Rubber Industry* **4**, 247–62(1928).—An illustrated review and discussion of present methods of manuf., of band (solid) tires, including the best compn. for the steel band, designs of bands, the character of the hard rubber base, methods of forming and attaching the tread, molding, vulcanizing, and electrolytic cleaning of molds. Tests to det. the detrimental *effect on the adhesion between bands and hard rubber of oil* showed that no trouble is likely to arise from the use of a sol. oil in machining. A general discussion follows the paper.
C. C. DAVIS

A simple tread-cracking test. A. H. NELLEN. Lee Tire & Rubber Co., Conshohocken, Pa. *Rubber Age* (N. Y.) **24**, 373–4(1928).—The *machine* described and illustrated is the first app. to measure the relative tendencies of different designs of treads to crack in service. A tire tread and carcass (with sidewalls and beads removed) runs as a belt at the speed desired over pulleys so arranged that multiple and exaggerated flexing takes place. Besides results of a mech. nature which were obtained, it was found that resistance to cracking may be enhanced by the use of special compounding ingredients, many of the most effective agents being powerful antioxidants. On the other hand, not all antioxidants inhibit cracking; in fact, there is probably no relation between antioxidant power and ability to improve resistance to cracking. C. C. D.

American practice in the manufacture of rubber-insulated conductors. RICHARD APT. *Kautschuk* **4**, 268–70(1928). C. C. DAVIS

Organic accelerators. WEBSTER NORRIS. *India Rubber World* **79**, 53–7(1929).—A review dealing with the development of org. accelerators of vulcanization, their classification according to the systems of Dinsmore and Vogt (*C. A.* **22**, 4273) and of Bloc (*C. A.* **22**, 4870), the phys. properties and the accelerating characteristics and peculiarities of 58 com. aldehyde-amines, thio acids, thiuramsulfides, thiazoles, thioureas, guanidines and miscellaneous org. salts, and finally recommendations for the use of particular accelerators for various types of rubber goods. C. C. DAVIS

The influence of zinc oxide on the coefficient of vulcanization. S. A. BRAZIER AND L. R. RIDGWAY. *J. Soc. Chem. Ind.* **47**, 351–6T(1928).—The present paper shows that erroneous values are often obtained when the coeff. of vulcanization is calcd. as the ratio of the difference between the total and free S and the rubber content. When ZnO and org. accelerators are present, there is more ZnS formed than has hitherto been supposed, in fact enough to render useless the ordinary method of calcn. of the coeff. of vulcanization. The expts. described deal with the effects on the extent of formation of ZnS and $ZnSO_4$ of: (1) increasing proportions of ZnO, for a const. rubber-S ratio; (2) various org. accelerators; (3) the time and temp. of vulcanization; (4) the addn. of fatty acids and of basic compds., *e. g.*, stearic acid, MgO, and CdO; (5) the type of rubber; and (6) the rubber-S ratio. The exptl. mixts. contained rubber 100, S 5, org. accelerator 0–1, ZnO 0–45. In unaccelerated mixts., the quantity of ZnS was very small, its quantity increasing both with the time and with the temp. of vulcanization. With diphenylguanidine but no ZnO, the max. coeff. obtained was 4.9, but with ZnO the max. coeff. was only 3.8. With diphenylguanidine the proportion of ZnS was in all cases 3–4 times as great as in the corresponding unaccelerated mixts. In general the ZnS increased both with the time and the temp. of vulcanization, and decreased with reduction in the S/ZnO ratio. Addn. of 1 part of MgO to rubber-S-diphenylguanidine-ZnO mixts. increased the rate of combination of rubber and S, and suppressed almost wholly the formation of ZnS. Aldehyde-ammonia behaved somewhat like diphenylguanidine, though without ZnO, combination of rubber and S was more rapid, and in some cases the free S was higher with ZnO than without it. In conjunction with the formation of appreciable quantities of ZnS, this showed that ZnO retards the chem. part of vulcanization. With tetraethylthiuramdisulfide, ZnO increased greatly the combination of rubber and S, with formation of only traces of ZnS. Zn isopropylxanthate acted like tetraethylthiuramdisulfide. It was decompd. during vulcanization, the Zn combining with the S, which conforms to the theory of Bruni and Romani that dixanthogen is formed and functions as the accelerator. The behavior of mercaptobenzothiazole was intermediate between that of the ultra-accelerators and the milder ones. Though it is supposed to be superior in an acid medium, the addn. of 0.5 part of stearic acid caused no appreciable change in the proportion of ZnS formed. Oleic acid did not influence the formation of ZnS except at high vulcanizing temps., where it reduced it. Preliminary expts. with CdO indicated that its behavior is similar to

that of ZnO, though in unaccelerated mixts. higher coeffs. were obtained, owing to a greater rate of combination of rubber and S. Analytical data on several technical mixts. are tabulated to show the errors encountered in detg. the coeffs. of vulcanization by calcn. from the free S only, instead of taking into account the sulfide-S. The older methods of detg. inorg. S compds. are not so reliable as that of Stevens (*J. Soc. Chem. Ind.* **34**, 244(1915); cf. *C. A.* **9**, 2466), particularly the $PhNO_2$ and paraffin disintegration methods. In some cases not all the rubber is removed by $PhNO_2$ and the insol. part contg. combined S remains with the inorg. S compds. Some transference of S from rubber to ZnO is possible during the heating with $PhNO_2$ or paraffin, a similar effect occurring in prolonged overcuring of mixts. vulcanized at high temps. In unaccelerated mixts. the ZnS is small enough to be ignored in calcg. the coeff. of vulcanization from the free and total S, but with some org. accelerators it upsets the results. The quantity of ZnS depends upon the % ZnO, the % S, the accelerator and other ingredients, and no general correction is possible. A small quantity, not over 0.1%, of $ZnSO_4$ was also formed. The results are of importance in relation to *specifications* which restrict the coeff. of vulcanization but allow the use of org. accelerators and ZnO.

C. C. DAVIS

Rubber patents in relation to the patents and designs acts. H. DOUGLAS ELKINGTON. *Trans. Inst. Rubber Industry* **4**, 336–42(1928).—The discussion refers to English law.

C. C. DAVIS

Practical method for obtaining dry air for humidity control in a rubber laboratory. F. S. CONOVER. N. J. Zinc Co., Palmerton, Pa. *Ind. Eng. Chem.* **21**, 162–4(1929).—Air previously dried by passage through silica gel is blown through the storage chambers. With 2 silica dehydrators, continuous drying is possible, the air being forced through one dehydrator while the other is being reactivated by treatment with air at 155–70°. Cooling and heating systems complete the equipment.

C. C. DAVIS

The mercury-vapor arc lamp. Its uses in a rubber factory. P. G. NAGLE. *Rubber Chemistry & Technology* **1**, 284–7(1928).—See *C. A.* **22**, 1251.

C. C. DAVIS

Researches on the structure of rubber. PAUL BARY AND ERNST A. HAUSER. *Rubber Chemistry & Technology* **1**, 401–9(1928).—See *C. A.* **22**, 4005.

C. C. DAVIS

The preparation of pure rubber from latex by means of alkali and its separation into sol-rubber and gel-rubber. RUDOLF PUMMERER AND HANS PAHL. Univs. of Erlangen and Greifswald. *Rubber Chemistry & Technology* **1**, 167–76(1928).—See *C. A.* **22**, 885.

C. C. DAVIS

Preliminary report on the coagulation phenomena and hydrogen-ion concentration in the latex of Hevea brasiliensis. N. H. VAN HARPEN. Algemeen Proefstation der A. V. R. O. S., Medan (Nederlandsch-Indië). *Arch. Rubbercultuur* **13**, 44–60(1929); (In English 61–77).—The lack of general agreement among theories explaining the nature of coagulation in *Hevea* latex led to a study by a different method in which the part played by the p_H value was particularly investigated. The H-ion concns. at the different stages of coagulation were measured by phys.-chem. methods by aid of the quinhydrone electrode. With this method, the irregular transition points of the coagulation process could be detd. with great precision. The transition point from the 2nd liquid zone to the 2nd coagulation zone appeared to occur at a p_H value of 0.80, and the transition point from the 2nd liquid zone to the 1st coagulation zone at a p_H value of 3.49. The transition from the 1st liquid zone to the 1st coagulation zone could not be fixed at a definite p_H value, for it varied between p_H 5.05 and p_H 4.77, depending upon the diln. of the latex. By the use of buffer solns. at the transition between the 1st liquid zone and the 1st coagulation zone, the existence of a flocculation zone with dild. latex was proved. This zone began at a p_H value of 5.05 and terminated at a p_H value of 4.77, beyond which point the flocculates coalesced to form a coagulum. When prepd. from fresh latex contg. no preservative, B liquid behaved abnormally in the 1st coagulation zone, in that no coagulation took place between p_H values of 4.77 and 3.49. On the other hand, with fresh latex, with latex preserved with NH_3 and with B liquid from ammoniated latex, coagulation took place in the normal manner between p_H values of 4.77 and 3.49. The occurrence of flocculation between the limits of p_H 4.77 and 3.49 with this B liquid prepd. from fresh latex cannot be explained by the absence of an enzyme (the coalase) but more probably can be explained by the inactivation of some unorganized chem. substance which normally causes flocculation at a p_H value of 4.77 and acts as a coalescing agent. It appears that a resinous substance in NH_4OH soln. not only causes flocculation at a p_H value of 4.78, but also begins its coalescing action at the same p_H value, and that very small quantities of this substance are sufficient to coagulate large quantities of latex. The supposition that the resinous substances which are present in latex, either as resinates or otherwise, are responsible for coalescence is very probable and further investigations on coagulation phenomena

should be directed into new fields on the basis of this hypothesis. When used a coagulant Na_2SiF_6 behaved in an unusual way, the p_H values being almost the same (3.25) at different concns., and the solns. acting like buffer solns. On titration Na_2SiF_6 behaved as if it had 4 available H ions, and therefore it can be considered as a combination of 2NaF + SiF_4, the latter hydrolyzing to $Si(OH)_4$ and 4HF. If so, a buffer soln. would form from the combination 2NaF.4HF. To prove this, the *dissocn. of HF at various concns.* at 26° was detd. The solns. were buffered with NaF. It was found that the concn. relationship in the buffer soln., *i. e.*, the ratios of the HF and NaF components, was 1. A test soln. contg. equal mol. concns. of HF and NaF was found to be a buffer soln. with a p_H value of 3.25. Na_2SiF_6 is dissocd. in water like a buffer soln. contg. 1 mol. of NaF and 1 mol. of HF. The strongly acid reaction resulting from the hydrolysis of Na_2SiF_6 can perhaps be best explained by the reaction: $Na_2SiF_6 + nH_2O \rightleftharpoons 2(NaF.HF) + SiOF_2(n-1)H_2O$. C. C. DAVIS

Making rubber goods of latex by electrodeposition. PAUL KLEIN. *Trans. Inst. Rubber Industry* **4**, 343–51(1928); cf. *C. A.* **23**, 1305.—App. and graphs are given showing the rate of deposition, deposition as a function of the c. d., the cond. and concn. of latex and stress-strain curves of the deposited product. C. C. DAVIS

Latex contaminated with copper compounds as a source of danger of fire. J. G. FOL AND W. DE VISSER. *Rubber Chemistry & Technology* **1**, 288–90(1928).—See *C. A.* **22**, 2078. C. C. DAVIS

The effect of heat on raw rubber in the presence and absence of air. J. D. FRY AND B. D. PORRITT. *Rubber Chemistry & Technology* **1**, 299–306(1928).—See *C. A.* **22**, 4870. C. C. DAVIS

Plasticity determinations in crude rubber. Influence of different factors on the changes in plasticity when keeping the rubber. O. DE VRIES. Rubberproefstation in Nederlandsch-Indië. *Rubber Chemistry & Technology* **1**, 291–8(1928).—See *C. A.* **22**, 3316. C. C. DAVIS

Plasticity and elasticity of rubber. A. VAN ROSSEM AND H. VAN DER MEIJDEN. *Rubber Chemistry & Technology* **1**, 393–400(1928).—See *C. A.* **22**, 3063. C. C. DAVIS

Color reactions of rubber. H. PAULY. *Rubber Chemistry & Technology* **1**, 361–3 (1928).—See *C. A.* **22**, 1703. C. C. DAVIS

Color reactions of rubber and gutta-percha. F. KIRCHHOF. *Rubber Age* (N. Y.) **24**, 555–6(1929).—English version of *C. A.* **23**, 544. C. C. DAVIS

Organic rubber colors. W. J. S. NAUNTON. *Rubber Chemistry & Technology* **2**, 99–107(1929).—See *C. A.* **22**, 4875. C. C. DAVIS

The effect of sunlight on the color of cured and of uncured accelerated mixes. R. DEFRIES AND W. J. S. NAUNTON. *Trans. Inst. Rubber Industry* **4**, 298–300(1928).—Rubber mixts. contg. crepe 100, ZnO 10, $BaSO_4$ 100 and S and accelerator (diphenylguanidine, di-*o*-tolylguanidine, triphenylguanidine, mercaptobenzothiazole, thiocarbanilide, aldehyde-ammonia, tetraethylthiuramdisulfide and Zn diethyldithiocarbamate) were exposed to ultra-violet light (1) before curing but not afterward; (2) only after curing, and (3) both before and after curing. These series of exposures were made independently in N and in O. With all accelerators, exposure before curing gave no visible effect, but after curing the samples so exposed were much darker than the unexposed samples. Furthermore, exposure of the cured samples lightened those which had not been exposed before curing, but failed to lighten those which had been exposed before curing. The discoloration was proportional to the time of exposure and varied with the accelerators. When the samples were irradiated in O before curing, the discoloration was only slightly more in O than on those irradiated in N before curing, while subsequent bleaching in O was far greater than in N. Ultra-violet light induces oxidation of the vulcanizates, which was supported by the fact that bleaching was also effected by H_2O_2. When the samples were undercured, the 2nd exposure to light intensified the darkening. The results indicate that (1) exposure of uncured samples causes a surface vulcanization; (2) the discoloration is an effect of a surface overcure produced by normal vulcanization superimposed on an already slightly vulcanized surface and (3) bleaching of vulcanizates by light results from oxidation, since it can be minimized by exposure in an inert gas and can be produced by oxidizing agents. When, however, there is an excess of vulcanizing agents to permit after-vulcanization, the subsequent exposure induces further darkening instead of bleaching. These effects also take place in sunlight, and it was their prevalence in technical mixts. which led to the more systematic expts. with ultra-violet light. C. C. DAVIS

The mechanism of the reënforcement of rubber by pigments. HARLAN A. DEPEW. N. J. Zinc Co., Palmerton, Pa. *Rubber Age* (N. Y.) **24**, 378–81(1929).—In a recent paper on pigment reënforcement as a function of resistance to tearing and resistance to cutting (cf. *C. A.* **22**, 3064), it was reserved for the present paper to explain

the mechanism of this reënforcement. Pigments may exist in rubber as: (1) soft pellets of undisintegrated pigment; (2) agglomerates of adherent massed particles; (3) dispersed particles, and (4) flocculated particles. (1) and (2) have no reënforcing effect; in fact they are in effect the same as porosity. If a fine pigment is not easily wet by rubber, there is a tendency to flocculate. The contrast between flocculation and dispersion (complete wetting) is illustrated by the familiar expt. of liquefying a stiff paste of ZnO and kerosene with a suitable agent (cf. Breyer, Rubber Division, *Am. Chem. Soc.*, Pittsburgh, **1922**; Bierer and Davis, *C. A.* **22**, 883). During the early stage of hot vulcanization rubber is semi-fluid and the ultimate distribution of the pigment is influenced greatly by this condition, both dispersion and flocculation proceeding during this stage of vulcanization. Flocculated pigment increases the hardness of rubber and therefore the resistance to cutting, while dispersed pigment increases the resistance to tear. Resistance to tear is increased by dispersed pigments because they act as obstacles in the path of the tear, so that the component of the force in the direction of tear is diminished. Accordingly with a fine pigment it is possible to increase the resistance to tear even when the bond between rubber and pigment is much weaker than the rubber itself. Hardness caused by flocculation is explained on the theory that the pigment assumes a rigid structure. When rubber is elongated, flocculated pigment and large particles cause uneven stresses which lower the reënforcing effect below that otherwise obtainable. ZnO is so easily wet by rubber that there is little tendency to flocculate regardless of the particle size. It does not, therefore, increase hardness, but tests show that the resistance to abrasion and to tear of mixts. contg. ZnO increases with decrease in the particle size of the ZnO. C. C. Davis

Specifications for rubber goods and the value of performance tests. J. M. Bierer and C. C. Davis. *Rubber Chemistry & Technology* **1**, 146–62(1928).—See *C. A.* **22**, 883. C. C. Davis

The direct molding of soft rubber scrap and the manufacture of soles. L. Graffe. *India Rubber J.* **77**, 222(1929).—English version of *C. A.* **23**, 545. C. C. Davis

New points of view in the analysis and classification of reclaimed rubbers. Eugenio Lindmayer. *Kautschuk* **4**, 278–80(1928).—In conjunction with the rubber content of a reclaim, its $CHCl_3$ ext. (after extn. with acetone) is a measure of the *degree of "devulcanization" of the rubber*. According to the theory of vulcanization already enunciated by L. (cf. *C. A.* **20**, 3837), the chief reactions of devulcanization are: $(C_5H_8)_6S(C_5H_8)_6 \longrightarrow (C_5H_8)_3S(C_5H_8)_3 + 2(C_5H_8)_3$ and $2(C_5H_8)_3 \longrightarrow (C_5H_8)_6$. From this, 51.65% of the originally sulfurated rubber would remain insol. in $CHCl_3$, while 48.35% would become sol. in $CHCl_3$. Though side reactions take place, this reaction is predominant enough so that the *degree of devulcanization* can be judged by the approach to this theoretical value of 48.35%. Examn. of 40 samples of reclaimed rubber of various types and from various sources showed a wide variation in this value. In no case did it exceed the theoretical 48.35% (which is termed "100% degree of devulcanization") while the nearest approach was a sample with a rubber content of 64.21%, which had a 94.59% degree of devulcanization. Detns. of the degree of devulcanization, *i. e.*, the relation between the $CHCl_3$ ext. and the rubber content, are useful in controlling reclaiming processes and in adapting a process to a particular type of raw material. In connection with the detn. of the rubber content, the C black content must also be detd., and no general method has been available. A *procedure* for detg. C black is described which is claimed to give excellent results. Finely divide the sample, ext. successively with acetone, concd. KOH and concd. HCl, wash with water, dry and incinerate in a combustion tube 80 cm. long (contg. $PbCrO_4$) in a Bunsen-Erlenmeyer furnace, as in regular org. analysis. From the quantities of CO_2 and H_2O, the C black may be estd. The C corresponding to C_5H_8 is considered to be the C in the rubber component, and therefore the C in excess of that corresponding to C_5H_8 is regarded as C black, and is calcd. merely by subtracting from the total C that contained in the C_5H_8 value. An idea of the proportion of bituminous substances may be had by a colorimetric examn. of the $CHCl_3$ ext. C. C. Davis

The history of "mineral rubber." Werner Esch. *Kautschuk* **4**, 252(1928); *Caoutchouc & gutta-percha* **25**, 14,233(1928).—Further comments on the origin of the term "mineral rubber" (cf. Luttringer, *C. A.* **22**, 4870). C. C. Davis

The history of "mineral rubber." A. D. Luttringer. *Kautschuk* **4**, 277(1928).—Comments on an article by Esch (cf. preceding abstr.). There is uncontrovertible evidence that the term "mineral rubber" was in common use in England a century ago to designate the natural product of Derbyshire. C. C. Davis

Methods for the purification of rubber hydrocarbons. Rudolf Pummerer and Hermann Miedel. Univ. Erlangen. *Rubber Chemistry & Technology* **1**, 163–6 (1928).—See *C. A.* **22**, 885. C. C. Davis

New derivatives of rubber. GIUSEPPE BRUNI AND E. GEIGER. Royal Polytech. Inst. Milan. *Rubber Chemistry & Technology* **1**, 177–81(1928).—See *C. A.* **21**, 4092. C. C. DAVIS

A new tetramethylbutadiene. A. D. MACALLUM AND G. S. WHITBY. McGill Univ., Montreal. *Rubber Chemistry & Technology* **1**, 341–5(1928).—See *C. A.* **22**, 2080. C. C. DAVIS

The gelatination of Vultex (appendix to the communication entitled "Dispersoidological investigations of latex"). P. P. VON VEIMARN. Imp. Tech. Res. Inst. Osaka (Japan). *Kolloid-Z.* **46**, 223–5(1928).—As was to be expected from the fact that the particles of vulcanized latex are less plastic than those of raw latex, the jelly obtained from vulcanized latex by a dispergator like LiI soln. is less adhesive and coherent than the corresponding jelly from raw latex. Expts. show, however, that under sufficiently great pressure the jelly from vulcanized latex acquires great elasticity and strength. When a film is obtained by evapn., capillary forces residing in the non-rubber components have the same effect as artificial pressure, the rubber contents of the particles combine, and the film shows a high elasticity. The view that the coherency depends upon the adhesion of the surface layers of non-rubber components is considered erroneous (cf. Hauser, *Latex*, 130). The plastic, strong films which surround latex particles consist of a mixt. of protein, resin, and rubber and have no more influence on the phys. properties of the rubber obtained by gelatination or coagulation than "active" fillers. The less the fibril structure of a coagulum is destroyed, the greater the elasticity of the coagulum. The plastic shells of latex particles become gelatinous and soft with dispergators of proteins and disintegrate on application of slight pressure. Therefore, in ordinary coagula which have undergone mech. treatment, the particles do not retain their individuality but disrupt, the rubber contents flowing together, and a fibril structure being acquired when the coagulum is stretched under suitable conditions. These fibrils in films or jellies from latex show a characteristic behavior, such as a tendency to form spiral masses when ruptured, and such great elasticity that they can be elongated to a point where they become invisible in the ultra-microscope. Six photomicrographs are included. C. C. DAVIS

A scheme for accelerator classification. R. P. DINSMORE AND W. W. VOGT. Goodyear Tire & Rubber Co., Akron. *Rubber Chemistry & Technology* **1**, 410–21 (1928).—See *C. A.* **22**, 4273. C. C. DAVIS

The reactions of aniline and its homologs as accelerators of vulcanization. TAKEO KIMISHIMA. *Rubber Chemistry & Technology* **1**, 307–40(1928).—See *C. A.* **22**, 1496. C. C. DAVIS

Problems of vulcanization. J. DUGUÉ. *Rev. gén. caoutchouc* **5**, No. 47, 9–12 (1928); cf. *C. A.* **22**, 2682, 3316.—Comments on articles by Bacon (cf. *C. A.* **22**, 3804) and by Bary (cf. *C. A.* **23**, 546). The point of view is taken that below its m. p., S can only be disseminated or dispersed in rubber and that none dissolves. Furthermore it is considered that S is not the vulcanizing agent, for it occurs in the same proportion in the phase of a vulcanizate which is sol. in C_6H_6 and in the phase which is insol. Vulcanized rubber is a mixt. of hard rubber ($C_{10}H_{16}S_2$) and raw rubber. Other features are discussed briefly. C. C. DAVIS

Some observations relative to the article of Dugué. PAUL BARY. *Rev. gén. caoutchouc* **5**, No. 47, 12–3(1928); cf. preceding abstr.—There is no exptl. evidence against and considerable evidence in favor of the soln. of S in rubber, and the chem. combination of S with rubber. C. C. DAVIS

The vulcanization of rubber. NICHOLAS BACON. Cornell Univ. *Rubber Chemistry & Technology* **2**, 138–60(1928).—See *C. A.* **22**, 3804. C. C. DAVIS

A new apparatus for vulcanization. E. A. HAUSER AND M. HUENEMOERDER. *Rev. gén. caoutchouc* **5**, No. 47, 16–7(1928).—See *C. A.* **22**, 4876. C. C. DAVIS

Temperature control in vulcanizers. C. B. MITCHELLA. Republic Rubber Co. *Rubber Age* (N. Y.) **24**, 547–8(1928).—A review and discussion. C. C. DAVIS

The influence of zinc oxide on the coefficient of vulcanization. S. A. BRAZIER AND L. R. RIDGWAY. *Trans. Inst. Rubber Industry* **4**, 301–12(1928).—See *C. A.* **23**, 1775. C. C. DAVIS

A comparison of the rate of combination of sulfur with rubber and the rate of vulcanization. E. R. BRIDGWATER. Du Pont de Nemours & Co. *Rubber Age* (N. Y.) **24**, 439–41(1929).—The object of the expts. was to ascertain why rubber cured with an org. accelerator to the optimum phys. state has a lower coeff. of vulcanization than rubber cured without such an accelerator, and why at the optimum phys. state the coeff. also varies with the org. accelerator. The problem was studied by curing to different extents rubber-ZnO-stearic acid mixts. with different proportions of S and of accelerators and detg. the combined S, the stress-strain curves and the power

to absorb C_6H_6. The results admit of several conclusions. The low combined S at optimum cure which is characteristic of mixts. with a high rate of vulcanization is ascribed to the combined effects of a stiffening or polymerizing action of the accelerator and the relatively small heat degradation in the short cures. With "Vulcanol" the rate of combination of rubber and S is slower and the rate of stiffening of the rubber mixt., *i. e.*, the progress of phys. vulcanization, is more rapid than with mercaptobenzothiazole. This difference can be explained only by the fact that some accelerators have a greater phys. stiffening or polymerizing effect than do others. Under the same conditions otherwise, accelerators differ in the influence which they have on the tendency of a rubber mixt. to absorb C_6H_6. Neither the stress-strain curve nor the combined S gives any information about this tendency to absorb C_6H_6. At any particular state of cure, the power to absorb C_6H_6 depends more upon the rate of vulcanization than upon the accelerator, and the higher the proportion of the latter the smaller is the absorption of C_6H_6. The small tendency of mixts. cured with a high proportion of S to swell in C_6H_6 is probably related to the high rate of vulcanization, for such mixts. with little tendency to absorb C_6H_6 have a low combined S content. In no case in the expts. did curing beyond the point of max. stiffness (judged by the stress-strain curve) diminish the power of absorbing C_6H_6. This absorptive power depends nearly as much upon the rate of vulcanization as upon the state of cure, a fact which is of importance in the formulation of *rubber mixts. to resist oil.* Such oil-resisting mixts. should be highly accelerated but not overcured. C. C. DAVIS

Some features of sulfur in rubber manufacture. DOUGLAS F. TWISS. *Rubber Chemistry & Technology* **1**, 346–55(1928).—See *C. A.* **22**, 2491. C. C. DAVIS

Devulcanization of rubber by formation of hexamethylenetetramine within the rubber. ANDRÉ DUBOSC. *Rev. gén. caoutchouc* **5**, No. 47, 14–5(1928).—An account of earlier expts. C. C. DAVIS

Devulcanization of rubber by accelerators or vitalizers. ANDRÉ DUBOSC. *Rev. gén. caoutchouc* **5**, No. 47, 13(1928).—An account of earlier expts. C. C. DAVIS

Latex, its preservation and concentration. A survey of the patent literature of recent years. ALADIN. *Gummi-Ztg.* **43**, 1047–9, 1105–6(1929); cf. *C. A.* **22**, 888.—Eighty-five patents are included. C. C. DAVIS

The "freezing" of raw rubber. I. A. VAN ROSSEM AND J. LOTICHIUS. Staatlicher Kautschuk Forschungs-Institut and Tech. Hochschule, Delft. *Kautschuk* **5**, 2–5 (1929).—The object of the investigation was to det. the nature of the changes which take place when rubber "freezes" and "thaws," *i. e.*, when it becomes hard and opaque at low temps. and subsequently becomes soft and elastic on warming. Measurements at increasing temps. of the d., hardness and light absorption of rubber which had been frozen for a long time showed a sharp decrease in all these values at 36–8°. There were no such breaks in the curves when rubber which had not been frozen was tested in the same way. These phenomena indicate that frozen rubber is partially crystd., and that the crystals fuse at 36–8°. This was further indicated by tests of the absorptive power of frozen and of unfrozen rubber for liquids, frozen rubber absorbing around 0.25 as much water as unfrozen rubber under similar conditions. Detns. of the *heats of swelling of frozen and of unfrozen rubber in PhMe* showed a difference which represented the *heat of fusion of the rubber.* The exptl. values of this heat of fusion varied but little with rubber from different sources and were 5.05 ± 0.28 cal. per g. of rubber. These values are not, however, the true value of the heat of fusion of cryst. rubber, for the proportion of cryst. rubber in frozen rubber was not known. This was in itself further evidence of partial crystn. Redetns. of the m. p. and of the change in d. on fusion of rubber kept frozen for 8 years showed an increase in the m. p. from 31–3° to 35–7° and a change in the decrease of the d. on fusion from 0.029 to 0.031. These changes probably resulted from the growth of crystals during the 8 years. When frozen rubber was heated to 100° and was then frozen again and maintained at 4° and at —10°, resp., the d. and the hardness increased slowly over a period of some days, the rubber at 4° requiring longer than that at —10° to reach the max. d. and hardness which it showed originally. When these frozen rubbers were warmed, the decrease in d. and in hardness indicated a wide fusion range which was complete at 12–14°. The expts. indicate that crystn. depends upon 2 factors: (1) the no. of cryst. nuclei, and (2) the growth of the nuclei. The no. of nuclei increases with the degree of supercooling. At 4° and at —10° there is a great no. of crystals of much smaller size than those in rubber preserved for years. The different proportion and size of the crystals explain why the "m. p." after thawing and refreezing differed so much from that of rubber frozen a long time. In general the m. p. increased with the time during which the rubber was kept frozen. Furthermore, the higher the temp. at which the rubber was kept frozen, the faster the growth of the crystals. Plasticizing rubber did not

influence the subsequent crystn. phenomena on freezing. **II. Röntgenspectrographic part.** J. R. KATZ. Univ. of Amsterdam. *Ibid* 6–9.—Röntgenographic examn. of rubber frozen under the different conditions described (cf. above) confirmed the existence of crystals, and the fact that the "freezing" of rubber is its crystn. There was no conclusive evidence that any appreciable polymerization or depolymerization accompanies the crystn. process. The tendency of crystd. rubber to become amorphous when swollen in an org. solvent renders the isolation of crystals a difficult problem.
C. C. DAVIS

Diffusion of water through rubber. EARLE E. SCHUMACHER AND LAWRENCE FERGUSON. Bell Telephone Labs., New York City. *Ind. Eng. Chem.* **21,** 158–62 (1929).—The rate of diffusion of water through rubber mixts. of various types was measured in 2 ways, in each case the rubber membrane being in contact with water on 1 side and a vacuum on the other; in 1 case the diffused water was measured by the vapor pressure of the water on the evacuated side, and in the 2nd case the diffused water was weighed after absorption by P_2O_5. From calcns. based on the data obtained the following formula was derived: $\log_e[p_0/(p_0 - p)] = KA/(V)t$, where p_0 is the vapor pressure of the water on the reservoir side of the membrane, p the vapor pressure on the evacuated side, K a const., A the area of the membrane, V the vol. of the evacuated chamber which the water enters, and t is the time. K may be regarded as the *diffusion const.* and depends upon the thickness of the membrane, its degree of satn., the temp. and the age of the rubber. The results of the measurements show that (1) the rate of diffusion of water through a rubber membrane is inversely proportional to the square of the thickness; (2) the rate of diffusion diminishes greatly as the hardness increases; (3) the effect of satg. the rubber with water is to increase the rate of diffusion, probably because there is not only an increase in the vapor pressure of the water within the rubber but also a decrease in thickness of the membrane and (4) there is no close relationship between the rate of diffusion and minor variations in the compn. of the rubber. The rubber samples which were tested included pale crepe, smoked sheet and rewashed smoked sheet all cured with S, ZnO, and an org. accelerator, rewashed smoked sheet cured with S, raw smoked sheet, pure rubber hydrocarbon, crepe low in protein cured with S and PbO, crepe treated with concd. H_2SO_4, hard rubber, a rubber-"thermoprene" mixt. cured with S, ZnO and org. accelerator, rewashed smoked sheet cured with S and PbO and heavily loaded with silica, an inner tube mixt. (smoked sheet, S, ethylidene-aniline, "mineral rubber," ZnO, and paraffin) and a white dental rubber.
C. C. DAVIS

A thermodynamic theory of rubber fillers. LOTHAR HOCK. Univ. Giessen. *Z. Elektrochemie* **34,** 662–4(1928).—It is shown that simple cases of reënforcement of rubber mixts. by fillers can be treated on a strictly thermodynamic basis. In developing a theory of the reënforcing action of fillers, like C black and ZnO, the free surface energy between rubber and filler must be considered responsible for the increased work of breaking the loaded rubber. Attempts were therefore made to find a means of detg. this free energy. When a rubber-ZnO mixt. is swollen in benzine, the accompanying heat tone is not the sum of the heat of swelling of the same quantity of rubber and the heat of wetting of the ZnO when these are measured separately, the difference representing the *heat of adhesion of rubber and filler.* It also represents the *total surface energy* and is therefore not a measure of the free surface energy. Furthermore, only part of the total surface of the filler comes into contact with the rubber because of incomplete wetting, and the greater the proportion of filler, the less nearly complete this contact. The *heat of wetting* is a function of the concn. of filler, and reaches its max. value at infinite diln. of the filler. It can be detd. calorimetrically in an approx. way by extrapolation to 0 concn. of the diminishing heats of wetting. Calling U_o the heat of wetting of 1 g. of filler when every particle is completely wetted, c the concn. of filler, and U_c the actual heat of wetting, U_c/U_o is the relative extent of actual surface contact. Thus with a rubber-C black (60–40) mixt., the heat of swelling is 0.1 cal. per g.; the heat of wetting of C black is 2.7 cal. per g. from which is calcd. a heat of swelling of the mixt. in benzine of 1.08 cal. per g. However, on account of the surface energy between rubber and C black, the observed heat of swelling was —0.15 cal., so that —1.23 cal. was the total surface energy. Therefore, U_{40} was 3.08 cal. per g. of C black. The increase in the work of rupture due to the filler is the free surface energy A and may be detd. from the work expended in breaking the material. However, with increasing proportions of filler, a work of friction must be overcome which is independent of free surface energy. Here, too, the limiting value A_o can be detd. approx. by extrapolation to infinite diln. Expts. showed that the order of magnitude of A_o/U_o is 0.5, *i. e.*, about 0.5 of the calorimetrically detd. total surface energy takes part in the reënforcement, though the ratio varies with different fillers.

It is thus possible to est. the phys. properties of a mixt. from a calorimetric detn. of the heat of swelling. That reënforcement depends upon free surface energy (contact surface tension δ multiplied by surface area of contact f) is supported by the fact that its temp. coeff. is of the same order of magnitude as the coeffs. of the surface tension of other 2-phase systems. Inherent difficulties in detg. A_e may be avoided by testing the same filler in 3 degrees of fineness, where the relative surface areas are known fairly closely. There are 3 different values of U_e, and f, nf, and mf are the surface areas per g. (where only n and m must be known) and k is the fraction of U_e which is equiv. to A_e, then: (1) $\delta f = kU_1$; (2) $\delta nf = kU_2$; and (3) $\delta mf = kU_3$; in which δ is the unknown. With U in abs. units, δ is calcd. directly in dynes. The theory therefore allows the calcn. of the surface tension between rubber and fillers in general. One equation is sufficient for calcg. δ, since microscopic measurements give the abs. value of f, and k can be detd. by expt. from A. The smaller the heat of swelling of the rubber, the more precise can U be detd. With freshly milled rubber it was 0.1 cal. per g. (in benzine), but after 9 months it was over 4 cal.; the great difference is probably caused by a *heat of aggregation* corresponding to the increase in the work of rupture during storage. Swelling does not break up this aggregation, and after drying and swelling again rubber gives the same high value. By detg. calorimetrically k, U_e, and U_c of a filler, and A_c by expt., it is possible to est. what proportion of the reënforcement results from the friction of the filler and what proportion from the surface energy, *i. e.*, what part of the reënforcement is of the ideal type. C. C. DAVIS

Chart for the estimation of equivalent cures. C. L. BRITTAIN. Gutta Percha & Rubber, Ltd., Toronto. *Ind. Eng. Chem.* **21,** 362–4(1929).—A graphical method is described for evaluating and comparing cures under conditions where the rise and fall of temp. play an important part in the integral cure. It is not limited, like the method of Sheppard and Wiegand (cf. *C. A.* **22,** 4272), to cures with a const. rate of temp. rise, and where the intensity of curing action is a const. function of temp. The method evaluates precisely the curing effect of a variable temp. schedule, no matter how irregular. It is also reversible, *i. e.*, a schedule with a certain desired curing effect may be obtained. There are 2 modifications of the method, depending upon whether abs. precision or an approx. result is desired. C. C. DAVIS

Effect of antioxidants in typical rubber stocks. MARION C. REED. B. F. Goodrich Co., Akron. *Ind. Eng. Chem.* **21,** 316–8(1929).—Natural and artificial aging tests of several different types of rubber mixts., including tire treads, inner tubes, footwear cured in dry air, sponge and steam hose, contg. the antioxidant "Agerite" are given. This substance improved the aging in all cases. C. C. DAVIS

Dispersoidological investigations. XXIII. Contributions to the dispersoidology of rubber. 1. The structure of jellies and of other coagula of ammonia-preserved Hevea latex and Hevea Vultex. P. P. VON VEIMARN, *et al.* *Rubber Chemistry & Technology* **2,** 108–37(1929).—See *C. A.* **23,** 1010. C. C. DAVIS

Contribution to the dispersoidology of rubber. P. P. VON VEIMARN. *Rev. gén. caoutchouc* **5,** No. 46, 3–8(1928); **6,** No. 48, 3–14(1929); cf. *C. A.* **23,** 2069.—A French version of *C. A.* **22,** 4872, covering only the structure of jellies and other coagula of *Hevea* ammoniated latex and Vultex. Twenty-six reproductions are included. C. C. DAVIS

Isomerization of rubber by electrical means (according to experiments by Guido Fromandi). LOTHAR HOCK. Univ. Giessen. *Z. Elektrochem.* **34,** 664–7(1928).—A summary of expts. by Fromandi (cf. *C. A.* **23,** 1009). C. C. DAVIS

The isomerization of rubber to cyclorubber under the influence of high-tension alternating currents. GUIDO FROMANDI. *Rubber Chemistry & Technology* **2,** 161–5 (1929).—See *C. A.* **23,** 1009, 1525. C. C. DAVIS

The question of priority in the discovery of thermoplastic gutta-percha-like, balata-like and shellac-like products from rubber and their classification. HARRY L. FISHER. U. S. Rubber Co. Labs., Passaic, N. J. *Kautschuk* **5,** 47–8(1929).—Polemical (cf. Kirchhof, *C. A.* **23,** 307). Evidence is presented to show that the claims of K. are without foundation. **Reply.** F. KIRCHHOF. *Ibid* 48. **Reply.** HARRY L. FISHER. *Ibid* 65. C. C. DAVIS

The accelerator "Tuads" and its imitations. FR. LÖBLEIN. *Kautschuk* **5,** 38–9 (1929).—Comments on an article by Esch (cf. *C. A.* **23,** 1526). Experience shows that "Thiuram" (a German com. grade of tetramethylthiuram disulfide) is quite similar to "Tuads" in its behavior as an accelerator. C. C. DAVIS

Comparative investigations of Thiuram (a Vulcacit product) and Tuads. A. VAN ROSSEM. Staatl. Kautschukprüfungsamt, Delft. *Kautschuk* **5,** 39–43(1929); cf. preceding abstr.—Analysis showed that "Thiuram" is purer than "Tuads," the latter contg. a trace of Mn and much higher ash and moisture contents. Comparative

tests of their accelerating activities in different types of rubber mixts. showed that in 2 cases the 2 products were virtually identical, while in another case the quality of the vulcanizate cured with "Thiuram" was superior. The relative tendencies to cause "scorching" were measured by keeping mixts. at 100° and then measuring their hardness and their swelling in C_6H_6. Scorching was greater with "Tuads." "Thiuram" is considered superior to "Tuads." C. C. DAVIS

Concluding remarks on the accelerator "Tuads" and its imitations. WERNER ESCH. *Kautschuk* **5**, 62(1929).—Comments on articles by Löblein and by van Rossem (cf. preceding abstracts). It is considered that the data presented by the above authors show the superiority of "Tuads" over "Thiuram" rather than *vice versa*. C. C. D.

Vulcanization and the structure of rubber. EUGENIO LINDMAYER. *Kautschuk* **5**, 35–8(1929).—The *sulfurization and oxidation of oils* and the vulcanization of rubber are explained in a hypothetical way by the aid of 3-dimensional space diagrams. No exptl. evidence is offered. C. C. DAVIS

The oxidation of vulcanized rubber. A. VAN ROSSEM AND P. DEKKER. Staatl. Kautschuk Forschungs-Institut, Delft. *Kautschuk* **5**, 13–21(1929).—The expts. represent a systematic study of the nature of oxidation of vulcanized rubber. A rubber-S (97.5–7.5) mixt. was cured to different degrees, the vulcanizates were finely divided, were then stored exposed to air in diffused light, and periodically up to 18 months their wts., acetone exts., free S, combined S, alc. KOH ext., oxidation products in the alc. KOH ext. and aq. exts. were detd. The alc. KOH exts. were detd. by swelling the acetone-extd. samples in C_6H_6, extg. with alc. KOH, filtering, washing, evapg. to a small vol., dissolving in water, acidifying and extg. with Et_2O. The products consisted of oxidation products and fatty acids from esters which were insol. in acetone. The alc. KOH ext. was a very sensitive *quant. measure of the extent of oxidation*, for it began to increase much sooner than did the acetone ext., reaching around 3 times its original value before the acetone ext. increased appreciably. The aq. ext. increased even more slowly than did the acetone ext. When oxidation was extensive, a part of the alc. KOH ext. was insol. in Et_2O, so that detns. were impracticable beyond a certain stage of oxidation. The proportion of oxidation products in the alc. KOH ext. was detd. by boiling the dried original alc. KOH ext. with 0.5 *N* alc. KOH, extg. the insol. residue with water and drying the raw residue at 100° (cf. Dekker, *C. A.* **21**, 195). A special investigation showed that (1) swelling with C_6H_6 was essential for accuracy in the detn. of the alc. KOH ext.; (2) equal parts of C_6H_6 and alc. should be used, and (3) if the sample swollen in C_6H_6 was extd. with alc. alone instead of alc. KOH, the oxidation products were extd. During the early stages of oxidation, the oxidation products were insol. in acetone, but were sol. in C_6H_6-alc. mixt. and in Et_2O. As oxidation progressed, products were formed which were sol. in the C_6H_6-alc. mixt. but not in Et_2O. Extn. with $CHCl_3$ after the acetone extn., and the temp. of drying of the alc. KOH ext. and of the oxidation products, were both without material influence on the detn. of the oxidation products. During oxidation the proportion of oxidation products increased much faster than did the total alc. KOH ext. The higher the combined S, the faster was the increase in the oxidation products during a given time of aging. This was also true of a rubber-S-ZnO vulcanizate. The alc. KOH ext. and the oxidation products of rubber-S mixts., 1 of which contained normal rubber and the other of which contained acetone-extd. rubber, were then detd. With the vulcanizates contg. normal rubber the proportion of oxidation products increased slowly with the degree of vulcanization, while with the vulcanizates contg. extd. rubber, it increased rapidly. The acetone ext. (minus free S) remained virtually const. throughout in each case. A large quantity of oxidation products were obtained by alc. KOH extn. of a rubber-S vulcanizate contg. acetone-extd. rubber, and purifying the KOH ext. with water. The mixt. was a brown, opaque mass with little elasticity, and insol. in C_6H_6, xylene, benzine, and Et_2O. Tabulated data give the ash, N, combined S, C, and H of the acetone-extd. rubber products from vulcanizates of different degrees of vulcanization, and show that the ash content of the oxidation products originated from the KOH treatment, that the oxidation products contained combined S, and that the products contained 3.7–5.2% O. When the cure was increased from 2 to 6 hrs., the oxidation products increased from 0.4 to 1.4%. In the same way a rubber-S vulcanizate (from acetone-extd. rubber) was analyzed after increasing times. The results are tabulated. After 2 weeks the alc. KOH ext. was no longer completely sol. in Et_2O. Both the Et_2O-sol. and the Et_2O-insol. portions contained combined S in smaller proportion than in the acetone-extd. vulcanizate. The Et_2O-sol. portion increased from 3.4 to 5.3% during the 8 months' aging. The Et_2O-insol. portions had higher O contents than the Et_2O-sol. portions after the same periods of aging. Expressed in terms of H/5C, the ratios of H to C in the acetone-extd. vulcanizates, in

the Et_2O-sol. and in the Et_2O-insol. portions of the alc. KOH exts. diminished gradually with the time of aging. This indicates that during oxidation H is oxidized out of the mol., probably as H_2O (cf. Kirchhof, *C. A.* **7**, 4083). In conjunction with the theory of Wieland (*Handbuch der Biochemie des Menschen und der Tiere*, 2nd Ed., 1925, II, 252), it is probable that H_2O is split off and condensation takes place with O as a bridge. Similar tests were also made of vulcanizates (acetone-extd. rubber-S) aged by the Geer oven method. The O contents of the Et_2O-sol. portions of the alc. KOH exts. increased in the same way as in natural aging, but the combined S contents were disproportionately low. Here again the ratios H/5C decreased slowly. The oxidation products were in turn oxidizable, their O content increasing rapidly on exposure to air. Changes in the alc. KOH ext. offer a sensitive *method of testing the aging of rubber products*, and of formulating *specifications for the aging properties of rubber products*. This is particularly true when mech. tests cannot be made.
C. C. DAVIS

Rubber manufacture. T. E. H. O'BRIEN. Rubber Research Scheme, Peradeniya. *Trop. Agr.* (Ceylon) **70**, 232–9(1928); cf. *C. A.* **22**, 1494.—Complete coagulation was obtained in some trials with Na_2SiF_6 when latex was diluted to 1.5 lb. per gal., but in other tests it was not complete. The coagulum was softer than that produced with AcOH. In both lab. and factory tests, entirely satisfactory results at 0.5 the usual cost were obtained with a suspension of 8 parts of Na_2SiF_6 in 1 part of HCO_2H and 1600 parts of H_2O, when the latex was diluted to 2 lbs. per gal. This soln. produced sheets remarkably free from bubbles, but it cannot be used with Al equipment. *p*-Nitrophenol added to the coagulant soln. at the rate of 0.025% by wt. did not affect the rubber in any observable way but largely prevented the development of fungi and molds, even under very adverse conditions. A. L. MEHRING

Balata in Para. FREDERIC M. BRAGA. *Bol. Agr. Ind. Com.* **2**, 428–35(1928).—Climatic conditions in the balata area, various species of *Mimasops* which yield balata latex, methods of extn. and market conditions are discussed, including data on products and exports. The following % analysis of British Guiana balata (crude and dry, resp.) was made at the Imp. College of Georgetown: moisture 1.9, –; gutta 49.7, 50.7; resins 44.0, 44.8; proteins 3.8, 3.9; ash 0.6, 0.9. S. L. B. ETHERTON

Use of rubber in the chemical industry. J. PANEM. *Rev. gén. caoutchouc* **6**, No. 49, 15–7(1929).—An illustrated description of recent development. C. C. DAVIS

Adsorption and diffusion of gases through rubber and through balloon fabrics. ANDRÉ DUBOSC. *Rev. gén. caoutchouc* **6**, No. 49, 14(1924).—A review (cf. *C. A.* **22**, 2078). C. C. DAVIS

The absorption of oxygen by rubber. G. T. KOHMAN. Bell Telephone Labs. *J. Phys. Chemistry* **33**, 226–43(1929).—The expts. deal with the absorption of O by raw and vulcanized rubber, and with the *relation between the rate of O absorption and natural aging*, the ultimate object being the development of an accelerated aging test. The influence of surface area on the rate of O absorption, the rate of O absorption as a function of the state of cure, the influence of the extent of milling on the rate of O absorption, the effect of antioxidants and of ozonized O on the rate of O absorption, the changes in tensile strength which result from the O absorption and the effect of heating in inert gases on tensile strength were studied. The *absorption app.*, which is described and illustrated, allowed the maintenance of a const. temp. and a const. O pressure. With rubber-S vulcanizates in O at 80°, expts. indicated that oxidation by O is autocatalytic and comprises at least 2 reactions, an addn. to the double bonds and a decompn. of the mol., the latter reaction continuing after the first was complete. The proportion of O absorbed was greater than the theoretical quantity to sat. the double bonds. With continuation of the reaction, the rate of absorption of O approached a const. value; water was formed, but almost no CO_2. When 0.02–0.05 mol. of O per $C_{10}H_{16}$ was absorbed, the vulcanizates became tacky, then weak; when they had absorbed 0.5 mol. of O, they lost their tackiness; with an absorption of 1.0 mol. of O they became hard and brittle. Surface checking was evident in some cases, this phenomenon being regarded as a preferential surface oxidation. At 80° the rate of absorption of O was noticeably influenced by the surface area per unit wt. when the area was small, but when the area was 40 or more sq. cm. per g., small variations in area were without much effect, probably because then the rates of diffusion of O were great enough to keep the rubber satd. with O. Expts. on the influence of the state of cure on the rate and extent of O absorption indicated that there was a close relationship between natural aging and O absorption at 80°, the same reactions probably occurring. The mechanism of O absorption by raw rubber differed from that by cured rubber, curing increasing both the rate and the proportion of O absorbed and changing the character of the absorption curve. The rate of absorption increased with the degree of cure. After cur-

ing, the relative rates of absorption of rubber milled to different extents indicated that O was absorbed during the milling process. Antioxidants have a neg. catalytic action rather than preferential absorption. In their presence the rate of absorption was retarded to an extent which varied with the concn. and the character of the antioxidant. In 1 case too small a proportion of an antioxidant hastened oxidation instead of retarding it. The character of the absorption of ozonized O differed considerably from that of pure O, the former being absorbed far more rapidly at first, but the rate diminished so that it ultimately became less than that of pure O. The reaction between rubber and ozonized O was not autocatalytic; the ozonized O apparently protected the rubber from the action of pure O, since the rate of absorption was much less in ozonized O, and on subsequent treatment with pure O the normal rate of absorption with the latter was not reached. Detns. of the relations between the proportion of absorbed O and the tensile strength of vulcanizates showed that as long as well-cured vulcanizates retained sufficient tensile strength to be of practical value, the deterioration was directly proportional to the proportion of O absorbed at 80°. When 0.5% O was absorbed, the tensile strength diminished nearly to 0.5 its original value. When undercured vulcanizates were heated in inert gases (N and CO_2), the tensile strength increased at first, as a result of further curing, but then diminished at a rate which was insignificant compared with that in O. In CO_2 the vulcanizates turned black, suggesting a reaction involving CO_2. The results in general indicate that natural aging is essentially a result of an absorption of atm. O. Forty-two references to closely related work are included. C. C. DAVIS

The standardization of rubber. FERDINAND BRÜGGEMANN. *Gummi-Ztg.* **43,** 1163–6(1929).—It is proposed to classify raw rubber not primarily according to its method of prepn. and superficial appearance but according to its cleanliness. Raw rubber would thus be divided first of all into (1) pure rubber, which is clean enough without washing for any ordinary use, and (2) crude rubber, which is contaminated with dirt sufficiently to necessitate washing. Plantation rubbers fall into each of these classes, depending upon their condition. Within these classes, rubbers are grouped according to whether they are prepd. by artificial or by natural coagulation and then in turn according to their thickness, color, general condition, origin, etc. C. C. D.

Some practical aspects of rubber evaluation. R. P. DINSMORE. Goodyear Tire & Rubber Co. *India Rubber World* **79,** No. 6, 77–8(1929).—There may be as great variation among individual bales of a lot of rubber or even within a bale as among different lots. As a result, blended batches vary day by day when tested experimentally in accelerated mixts., in tread and solid tire stocks, etc.; this variation also holds true under service conditions. Ordinary methods of blending are not effective in minimizing to a satisfactory extent this normal variation, and the only advisable procedure is to mass as much rubber as practicable on mills, to test each batch and to classify the batches as high-, medium-, and low-grade. These individual grades are then used in different rubber formulas in which each is most suitable. In testing the batches, modulus tests of formulas, which have been found to be reliable criteria of the behavior in service of the factory stocks concerned, are essential, but short cures at high temps. with cold water conditioning make complete control tests possible in 25 mins., *i. e.*, within practical working limits. C. C. DAVIS

Rubber as it is revealed by x-rays. G. L. CLARK. Univ. of Illinois. *India Rubber World* **79,** 55–9(1929).—C. shows that unstretched rubber gives broad diffraction haloes characteristic of "amorphous" substances, but that stretched rubber gives a diffraction pattern characteristic of cryst. substances. He then tabulates the essential exptl. facts derived from x-ray studies of rubber by Katz, Hauser and Mark, Feuchter, Meyer and Mark, Clark, and others. Natural rubber in practically every state, *e. g.*, coagulated latex, crepe, smoked sheet, or vulcanized sheet, produces a cryst. diffraction pattern on stretching, whereas synthetic rubber does not. The initial appearance of a pattern is at about 75% elongation for raw rubber and above 250% for vulcanized rubber. The intensity of the diffraction spots increases linearly with increasing elongation, while the intensity of the broad halo decreases simultaneously. The positions of the interferences are const. with increasing elongation, while their breadths are const. with increasing elongation to at least 800%. The size of colloidal micelles may be calcd. When stretched isothermally, *i. e.*, very slowly, the interferences are very faint or absent, but when stretched adiabatically, *i. e.*, very rapidly, the interferences attain their max. intensity at the same elongation. The pattern appears instantaneously on stretching, and it disappears at about 60°. The pattern disappears on releasing the tension, though sometimes it persists some time after release, especially if the specimen is cooled after stretching. Stretched specimens placed in solvent vapors no longer produce cryst. diffraction patterns. By "racking," rubber can be stretched 10,000%, and it

then gives as sharp a diffraction pattern as do pure org. compds.; it is insol. or largely non-swelling in the usual org. solvents. Extd. rubber, free from resins and proteins, gives the pattern on stretching. The positions and appearance of the interferences are independent of the botanical source. "Frozen" rubber gives sharp concentric rings corresponding to the same spacings as the interferences of stretched rubber. These sharp rings are replaced by broad haloes on warming the specimen. Cryst. fillers give characteristic patterns, usually with a random arrangement of the filler crystals, while the usual rubber pattern also appears. Calendering introduces a fibrous structure detected by x-rays even without stretching. Mastication tends to destroy the cryst. orientation even when strongly stretched. Synthetic rubber and rubber-like polymers produce broad "amorphous" haloes, which remain unchanged up to the highest elongations, though some workers have noted slight changes in some of these patterns, especially at low temp. Orientation apparently occurs in 1 or 2, but not in 3 dimensions. Dimensions calcd. from the "amorphous" pattern of unstretched rubber give values of 14.88 (inner ring) and 6.05 A. U., while very pure extd. rubber gives values of 11.15 and 5.97 A. U. The presence of a solvent increases the former to 14.76 A. U. The inner ring is characteristic of polymers. The most accurate values show the unit cell to be rhombic, $a = 12.3$, $b = 8.3$, $c = 8.1$ A. U., contg. 8 C_5H_8 groups. The colloidal micelle seems to have the shape of a long flat bundle, contg. 10,000 to 20,000 unit cells, or 80,000 to 150,000 C_5H_8 groups. C. points out that though the unit cell contains only 8 C_5H_8 groups, this is not a contradiction of the large mol. wt. The unit cell here, as in the polyoxymethylenes (Hengstenberg, *Z. physik. Chem.* **126,** 425 (1927)), contains only part of the true chem. mol., the long chain mol. extending through many adjacent unit cells. This chain-like mol., bound by primary valences, is estd. to contain 75 to 150 C_5H_8 groups. These results indicate a very long, preformed mol., in which the C_5H_8 "links" lie on screw axes. In a stretched condition these chains lie parallel, giving a cryst. structure. In the unstretched state they coil and lose the parallel arrangement, resulting in "amorphous" x-ray diagrams. Elasticity is due to ethylenic linkages. Vulcanization, in removing double bonds, should ultimately result in hard rubber without elasticity and in an increase in size of the colloidal micelle. Recent work by C. fully verifies this increase in particle size. G. R. Y.

Rubber structure research and its bearing on the elastic properties of colloids in general. E. A. HAUSER. Metallgesellschaft, A.-G., Frankfurt. *Ind. Eng. Chem.* **21,** 249–51(1929).—Recent research on the structure of rubber is discussed from 3 points of view: (1) the isolation of 2 components, (2) the transformation of 1 component into the other, and (3) interpretations of the structure from x-ray data. It is suggested that all fibrous substances are constituted of main valency chains bundled together by micellar forces to form parcels of parallel chains. The *elasticity* will depend largely upon the form of the smallest element, whether this is a ring as in cellulose or a straight chain as in rubber, and especially upon the helix angle. The appearance of x-ray fiber diffraction patterns depends upon the condition of these chains, *i. e.*, whether or not they are swollen. Thus, stretched rubber in solvent vapors loosens the pattern. *Celluloid* is analogous to rubber, for when unstretched, it gives an "amorphous" scattering, since the nitrocellulose has been swollen by the camphor. Whenever elastic stretch compensates for plastic internal flow for a sufficient time, and the viscosity of the lower polymerized phase does not prevent orientation (producing an inelastic product as with many resins), a similar x-ray diffraction pattern is obtained. This has been proved for *gelatin*, other *jellies*, and *polymerized oils* in still unpublished work. C. C. D.

Report of the raw rubber specifications committee. ELLWOOD B. SPEAR, *et al. Ind. Eng. Chem., Anal. Ed.* **1,** 55–6(1929).—Comparative tests of 2 different rubber mixts. by 4 industrial labs. and 1 univ. lab. are given to show the wide variations in the results obtained when the same rubber was distributed to the various labs. The 2 series of vulcanizates were prepd. and tested under conditions as nearly identical throughout as possible. C. C. DAVIS

Hard-rubber dust and one of its recent developments: direct grinding of the dust. FRANK A. BATH. *Caoutchouc & gutta-percha* **25,** 14,222–4, 14,262–3(1928).—Descriptive, with particular reference to the patented process of Rissik-Fraser & Co. C. C. DAVIS

The recovery of volatile solvents by the system of A. Boecler. A. BOECLER. Bensin Condensation Syst. Boecler, Malmoe (Sweden). *Rev. gén. caoutchouc* **6,** No. 49, 18–20(1929).—An illustrated description (cf. *C. A.* **22,** 2493). C. C. DAVIS

Electrical behavior of rubber-sulfur compounds. DONALD W. KITCHIN. Simplex Wire & Cable Co., Boston. *Rubber Age* (N. Y.) **24,** 671–2(1929).—The observation of Curtis, McPherson, and Scott (cf. *C. A.* **22,** 330) that power factor and dielec. const. maxima correspond to simple chem. compds. is without significance, for by changing

the test frequency the maxima can be shifted over a wide range of compn. Boggs has suggested that certain rubber-S compds. are dipole mols. and that, though the raw rubber mol. is electrically neutral, formation of an unsymmetrical rubber-S mol. would produce a dipole, while further addn. of S to form a symmetrical mol. would involve loss of dipole properties. With a low proportion of S, probability favors the formation of dipole mols., while increase of S increases the probability of compensation, and the compn. indicated by the proportion of combined S at max. power factor or dielec. const. would not correspond to the mol. of max. dipole moment. With increase of combined S from O, the power factor and dielec. const. should increase to a maxima, and then diminish. The dipole power loss would arise from a heat loss from motion, but the mols. would be held by elastic forces, so that in a changing field the surrounding medium would undergo rapid stretch and release. In rubber this would cause friction losses evidenced as elec. power losses. Moreover, with increasing S, the rubber becomes more rigid, so even if the no. of dipoles remained const., the motion would change greatly with changing compn. Vulcanized rubber offers, therefore, a more complicated problem than liquids. However, there should be a characteristic frequency for each compn. in the range where dipole mols. exist, and the softer the rubber the higher this frequency. The higher the applied frequency, the lower the S content at which the max. power factor and dielec. const. should occur, which is shown by means of curves to be true. A progressive decrease in the max. dielec. consts. with increasing frequencies is explained by the fact that from O to 14% S the no. of dipoles increases nearly linearly, and that, though there are more dipoles at 10 than at 6% S, the dielec. const. for 380,000 cycles is greater at 6% S (the stiffness at higher S contents being too great for dipole response). Even a d. c. test probably does not show the compn. at which the max. no. of dipoles are present, for at high S contents the speed of orientation may become so low that the d. c. test does not permit full orientation. Such studies are important because they may aid in explaining the nature of vulcanization. C. C. DAVIS

The production of glossy spread rubber goods by the aid of vulcanization in ultra-violet light. RUDOLF DITMAR. Kautschuklaboratorium, Graz. *Gummi-Ztg.* **43,** 1172(1929).—The process of Bernstern for curing rubber mixts. at relatively low temps. in ultra-violet light (cf. *German Patent* 262,708, Class 39b, Gr. 3(1912)) must be carried out in an inert gas or *in vacuo* to prevent oxidation by the O_2. Expts. show, however, that if tetramethylthiuramdisulfide is used as an accelerator to minimize the curing time and therefore the exposure, and Se red (cf. D., *C. A.* **23,** 1526) as a protective agent, the spread material may be cured in air. Thus, the mixt. rubber 100, S 3.5, tetramethylthiuramdisulfide 2, $ZnSO_4.5NH_3$ 7, $Na_2S_2O_3$ 2, Se red 1.8, TiO_2 2, is dissolved in C_6H_6, spread, dried, and exposed to ultra-violet light for a few mins.; the rubber is thoroughly cured and acquires a high gloss. C. C. DAVIS

Rubber roadways. T. H. CHAPMAN. Rubber Roadways, Ltd. *Rubber Age* (London) **9,** 439–43(1929).—A review and discussion, dealing with road-surfacing materials in general use, difficulties in new surfaces, a survey of past exptl. roadways and the results, and future prospects. C. C. DAVIS

Problems of vulcanization. J. DUGUÉ. *Rev. gén. caoutchouc* **6,** No. 49, 13(1929).—A reply to Bary (cf. *C. A.* **23,** 2070). Further comments on the subjects already discussed are added. C. C. DAVIS

Isoprene and rubber. XIII. Constitution of rubber. H. STAUDINGER, M. ASANO, H. F. BONDY, AND R. SIGNER. *Ber.* **61B,** 2575–95(1928); cf. *C. A.* **21,** 1371.—The evidence in favor of the Pummerer and the Staudinger views on the constitution of rubber is briefly reviewed. Against P.'s views the authors contend that: (1) Crystn. of a compd. is no proof that it is homogeneous and of low mol. wt.; the mixt. of polymeric-homologous polyhydroxymethylenes crystallizes just like homogeneous polyhydroxymethylene diacetates of low mol. wt. (2) A hydrorubber, $(C_5H_{10})_8$, distg. without decompn. does not exist; on distn. of the hydrorubber, which has a much higher av. mol. wt. (3000–5000), it undergoes cracking with the formation of a mixt. of unsatd. hydrocarbons. (3) Repetition of the mol.-wt. detns. in menthol shows that mol.-wt. detns. can be carried out only with great difficulty in this solvent with its extraordinary slowness in crystn.; crystn. after addn. of the substance under investigation must be approx. as rapid as that of the pure solvent and care must be taken that the outside temp. remains const., whereas addn. of rubber slows up the velocity of crystn. extraordinarily and considerable heat is lost to the surrounding bath, after the supercooling, so that very widely varying depressions of the m. p. are obtained. Similar observations were made on a cyclorubber having in C_5H_8 an av. mol. wt. of 8500; in menthol it gave a value of 150. Expts. with paraffin hydrocarbons and paraffin hydrocarbon mixts. of high mol. wt. showed that the Rast method is well adapted to the detn. of the mol. wt. of such stable hydrocarbons and hydrocarbon mixts. The values obtained by Pum-

merer, Nielsen, and Gündel with rubber were in the main confirmed, *i. e.*, values between 1000 and 2000 were obtained, but that slight decompns. occur at these high temps. was shown by the fact that the camphor subliming over has a lower m. p. than pure camphor; moreover, cyclorubbers, whose mol. wts. in C_6H_6 agree with their phys. properties (m. p., soly., viscosity of the soln.) show in camphor appreciably lower values. Association in C_6H_6 seems excluded by the fact that the same values are obtained at different concns., and when these cyclorubbers are recovered from the camphor, they show in C_6H_6 the same values as before; the viscosity of the C_6H_6 solns. is likewise not altered by previously dissolving the cyclorubbers in camphor. The lowering in the m. p. of the sublimed camphor is ascribed to contamination by volatile products of low mol. wt. resulting from the breaking down of O-contg. impurities in the camphor; when the rubber is recovered from the camphor, these volatile products remain dissolved in the alc. and therefore do not affect the mol. wt. in C_6H_6 of the recovered rubber. (4) Isorubber-nitrone is not, as assumed by P., a homogeneous substance but a mixt. of polymeric-homologous products resulting from the breaking down of the rubber with PhNO. (5) Röntgenographic investigations cannot prove the existence of a small basic mol. The authors therefore hold to their view that rubber consists of macromol. polymeric-homologous polyprenes. The results of mol.-wt. detns. of cetyl alc., cholesterol, cyclorubber and rubber in menthol, and of paraffins, paraffin mixts., rubber and gutta-percha in camphor are reported. C. A. R.

Natural and synthetic rubber. I. Products of the destructive distillation of natural rubber. THOMAS MIDGLEY, JR., AND ALBERT L. HENNE. Cornell Univ. *J. Am. Chem. Soc.* **51**, 1215–26(1929).—Light pale crepe rubber was destructively distd. at atm. pressure, the temp. of the bath being raised as quickly as possible to 700° (to obtain a favorable yield of isoprene). Addn. of Mg to the rubber greatly increased the yield of substances other than isoprene and dipentene; Zn, Fe, and Al have a similar effect but to a very much smaller extent; Cu is without effect; brass is the same as Fe. In the distns. the same components were found but in different proportions. A table gives the yields of the 2 distns. No fully satd. compd. was detected. The following compds. were isolated by fractional distn. of the reaction product after the removal of the isoprene (the phys. consts. and methods of identification are given): 3-methyl-1-butene, 2-methyl-1-butene, isoprene, 2-methyl-2-butene, a *2-methylpentene*, b. 59–60°, d_{20}^{20} 0.730, n_{20} 1.4117; 3-methyl-2-pentene; a *3-methylpentadiene*, b. 76–9°, d_{20}^{20} 0.742, n_{20} 1.4346; C_6H_6, a *compd.* b. 93–5°, d_{20}^{20} 0.744, n_{20} 1.422; Δ^3-tetrahydrotoluene, Δ^2-tetrahydrotoluene; a *fraction* b. 109–10°, d_{20}^{20} 0.783, n_{20} 1.4413; Δ^1-tetrahydrotoluene, PhMe; a *fraction* b. 121–2°, d_{20}^{20} 0.765, n_{20} 1.4287, probably 2-methylheptene; $\Delta^{1,3}$-*dihydro-m-xylene*, b. 129–30°, d_{20}^{20} 0.795, n_{20} 1.4451; *m*-$C_6H_4Me_2$, *p*-tetrahydroethyltoluene; a *fraction* b. 158–9°, d_{20}^{20} 0.834, n_{20} 1.4665; *p*-EtC_6H_4Me; a *fraction* b. 162–3°, d_{20}^{20} 0.828, n_{20} 1.46, analyzing for $C_{10}H_{18}$; a *dimethyloctadiene*, b. 162–3°, d_{20}^{20} 0.8105, n_{20} 1.456; dipentene. Assuming that the Staudinger formula is correct, that the single bonds farthest from the double bonds are the weaker spots and that the formation of 6-C rings is favored, it has been shown that nearly all of the compds. actually isolated could be predicted. **II. Reduction of isoprene by Na-NH_3.** *Ibid* 1293–4.—Reduction of isoprene with Na in liquid NH_3 gives 60% of 2-methyl-2-butene. High mol.-wt. hydrocarbons were formed but were not investigated. **III. Dimethyloctadiene.** *Ibid* 1294–6.—Well-purified isoprene, active toward polymerization, was placed in contact with metallic K; EtOH was added slowly at a rate just sufficient to give a moderate evolution of H at the surface of the K; there resulted a mixt. of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes, b. 163–7°, d_{20}^{20} 0.769, n_D^{20} 1.4457. The constitution of the mixt. was detd. by oxidation with CrO_3 in AcOH. This reaction indicates that the mechanism of the polymerization of isoprene to synthetic rubber is the joining of many isoprene mols. by linkage of the 1,1-, the 1,4-, or the 4,4-C atoms to produce a long chain mol. C. J. West

The physical properties of rubber. MARTINN RUHEMANN AND FRANZ SIMON. Berlin. *Z. physik. Chem.*, Abt., **138A**, 1–20(1928).—The change of a supercooled liquid to an amorphous solid is not continuous, but occurs within a definite temp. interval. With glycerol, for example, this is shown by an anomaly in the sp.-heat curve, the value of the sp. heat falling off much more rapidly within this interval than in the neighboring temp. regions. This same anomaly in the sp.-heat curve, which R. and S. call the α anomaly, was found in smoked sheet, where the change to a "glassy" solid with falling off of elasticity took place between —65° and —80°. With synthetic rubber the change was between +5° and —12° for methyl rubber H, and between —5° and —22° for methyl rubber W. A second anomaly, referred to as β, was found as a peak in the

sp.-heat curve for natural rubber at about 0°, and was not easily reproducible. The behavior of the coeff. of expansion in this temp. range showed that this could not be due to the presence of H_2O. "Patent rubber," pure, raw rubber, masticated, pressed several days at 150 atm. at —15°, gave the same α and β anomalies, though β was less pronounced. "Frozen" smoked sheet and "patent rubber" gave the α and β effects, also peaks (called the γ anomaly) at +25° and +17°, corresponding to 4 cal. and 6 cal. per g. of rubber, resp. Since the opalescence vanished, and immediate cooling and rewarming showed no γ effect, this is taken as the heat of fusion of the crystallites shown by x-ray photographs to be present in frozen rubber. Smoked sheet, racked 500% at 55°, showed α and β anomalies, but up to 35°, no γ, though the opalescence of the sample indicated that the "m. p." had not been reached. A sample racked 400% at 35° gave the γ effect, the max. of the peak being at 34°; the rubber thus "melted" was clear and elastic. The total-, gel- and sol-rubbers of Pummerer (*C. A.* **22,** 885) showed the α and β anomalies. Rubber as a 2-phase system might be expected to show 2 α anomalies. The absence of a second anomaly is explained by the fact that the more viscous phase is in the "glass" state to above 30°, and hence the second α effect was not detected in these expts. The (purely speculative) explanation advanced for the β anomaly is a further polymerization and attending solidification to the "glass" state. G. R. Y.

The "degree of devulcanization" and the evaluation of reclaimed rubbers. HEINRICH LOEWEN. *Kautschuk* **5,** 61–2(1929).—Comments on an article by Lindmayer (cf. *C. A.* **23,** 2069). So-called reclaiming does not represent true devulcanization, but plasticization, for devulcanization would involve the complete removal of combined S. The concept of devulcanization of L., whereby vulcanized rubber splits into a component rich in S and a component free of S, is contrary to all facts of org. chemistry and is not supported by exptl. data. All that can be said is that an increase in the $CHCl_3$-sol. component is accompanied by an increase in plasticity. The "degree of devulcanization" on the basis proposed by L. is fallacious, for it signifies that only 0.5 of the rubber can become sol., an assumption without foundation. The suggestion of L. is of more practical than of theoretical significance. C. C. DAVIS

The use of "Catalpo" in the rubber industry. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **26,** 14,389–90(1929).—A description of the characteristics of "Catalpo" clay. C. C. DAVIS

The aging of rubber. Its preservation. F. JACOBS. *Caoutchouc & gutta-percha* **26,** 14382–3(1929); cf. *C. A.* **22,** 4876.—A review with special reference to work by Villey and Vernotte (cf. *C. A.* **19,** 1208). No artificial aging method duplicates natural aging in darkness. Furthermore, it is considered that the deterioration of vulcanized rubber is an unnecessary change, in that mixts. of suitable compn. and vulcanized to the proper condition deteriorate little or not at all. C. C. DAVIS

Ornamented rubber. JOSEPH ROSSMAN. *India Rubber World* **80,** 61–4(1929).—An illustrated review of U. S. patents relating to methods of designing and coloring. C. C. DAVIS

The cleavage of stretched rubber and the distortion of its cleavage planes by compounding. M. LE BLANC AND M. KRÖGER. Leipzig. *Z. Elektrochem.* **34,** 725–34 (1928).—Whereas a cryst. substance undergoes a distortion of lattice on stretching, rubber must first gain a cryst. structure, which may then undergo distortion and breakage. The introduction of compounding ingredients causes a distortion of the lattice; at low temp. in rubber not contg. compounding ingredients, part of the rubber itself may act in this capacity. A microscopic examn. of the cleavage faces of various rubbers shows that: (1) the finer the compounding ingredient, the more the places of distortion of the planes, and (2) the greater the energy of adsorption of the compounding ingredient, the greater is this distortion. A scheme is given showing the interrelation of various forms of rubber (raw, compounded, vulcanized, etc.) Stress-strain data at various temps. are given for artificial isoprene rubber, and for 15 and 30% admixts. of KCl, NH_4Cl, B_2O_3, KBr, KSCN, ZnO, $MgCO_3$, BaO_2, $BaSO_4$ and for 15% admixts. of methylene blue, eosin, furrol B, furrol GB and rhodulin orange. The diam. of the testing ring has an influence on the stress-strain curves and breaking point, the breaking value being greater for a smaller ring than for the usual 44.6 mm. ring of the Schopper machine. Tables show results of these tests. G. R. Y.

A temperature-recording micropress for studying the course of vulcanization. JAMES C. WALTON. Boston Woven Hose & Rubber Co., Cambridge, Mass. *Ind. Eng. Chem., Anal. Ed.* **1,** 106–8(1929).—A new temp.-recording electrically-heated micropress for use in studying vulcanization microscopically is described and illustrated (cf. Dannenberg, *C. A.* **21,** 3764; Hauser and Hünemörder, *C. A.* **22,** 4876; **23,** 2070). This instrument permits the duplication of press cures on a very small scale and makes

it possible to det. the temps. at which various changes take place during the progress of vulcanization. With the aid of this app., the *vulcanization of several rubber mixts. with and without S* was studied microscopically. It was found that after curing a rubber-S-PbO mixt. there is no crystn. of the free S, even when the cure is very brief. Both m-$C_6H_4(NO_2)_2$ and benzyl peroxide vulcanize rubber in the absence of S. The former requires an activator like PbO (diphenylguanidine being ineffective), and does not crystallize from vulcanized mixt., where benzoyl peroxide does not require an activator, and it crystallizes from the vulcanized mixt. in a manner very similar to S. Photomicrographs of rubber before and after vulcanization by m-$C_6H_4(NO_2)_2$ are included.
C. C. DAVIS

The vulcanization of rubber by sulfur chloride. J. SOUDIER. *Caoutchouc & gutta-percha* **26,** 14,389(1929).—It is claimed that substances have been found which in very small proportions will accelerate the cold vulcanization of rubber by S_2Cl_2 and give products of superior quality. They are not named. C. C. DAVIS

Plasticization and plasticizing agents. PAUL BARY. *Caoutchouc & gutta-percha* **26,** 14,464–8(1929).—A discussion of the phenomena and of the mechanism of plasticization in its relation to the chem. theory of colloids. Swelling of a colloid involves 2 distinct phases, (1) *penetration* of the liquid, accompanied by an increase of vol., and (2) *solvation*, which may proceed as far as complete colloidal soln. The mols. of the colloid are highly polymerized, and are previously solvated. Penetration, therefore, is aided by this initial solvation, though the liquid has insufficient affinity to rupture the mols. and to produce further solvation. For plasticization to accompany swelling it is necessary that: (1) the colloid be swollen enough to be elastic and deformable under pressure; (2) the liquid contain the elements of solvation to such a degree that the jelly fuses at a definite temp. and (3) this m. p. is close to the working temp. Plasticization requires the expenditure of energy corresponding to the depolymerization which takes place, and this expenditure is counterbalanced (in part or wholly) by the heat evolved in the partial combination of the solvent at the points of mol. rupture. When the heat of solvation exceeds that of depolymerization, there is a reduction in the degree of polymerization, even to complete soln. However, liquids which swell colloids best are not always those with the greatest solvating power, but those which, without solvating the colloid appreciably at ordinary temp., begin their action at slightly elevated temps. On recooling, there should be repolymerization and desolvation. Assuming that rubber is solid α form and a liquid β form dissolved in the α form to produce a jelly, rubber may be considered to be an auto-plasticized substance. When polymerization of the isocolloid reduces the proportion of the β form, the plasticity diminishes. There is no essential difference in this rubber jelly and other jellies of 2 dissimilar components unless, as seems probable, there are solvating agents present in the rubber, *viz.*, its resinous and protein impurities. If these impurities act as solvating agents, it is one of the reasons why synthetic rubbers have not so much elasticity as natural rubbers. In general, then, a substance is plastic only if it has 2 components: (1) a colloid capable of swelling and (2) a liquid sol. in this colloid and with the power of solvating the latter. This liquid can be a mixt. of 2 or more liquids, with differing powers of solvation, and therefore, lending different degrees of elasticity to the resulting plastic mixt.
C. C. DAVIS

Patents

Accelerator of vulcanization. JAN TEPPEMA (to The Goodyear Tire and Rubber Co.). Can. 286,103, Jan. 1, 1929. Reaction products of certain aromatic aldehydes, particularly the aldehydes having a hydroxyl group substituted in the aromatic nucleus, and amines, such as aniline or toluidine, when incorporated in a rubber compd. materially accelerate the rate of vulcanization and impart desirable characteristics to the product. An example of such reaction product is obtained by the interaction of β-hydroxynaphthaldehyde and aniline. One method of prepg. this product is to intermix mol. quantities of β-hydroxynaphthaldehyde and aniline, and heat under a reflux condenser for several hrs. A yellow cryst. compd. is obtained which upon being heated gives off an oil and leaves a resinous mass. The latter material is a desirable accelerator, whereas the yellow cryst. product has little, if any, accelerating properties.

Rubber. THE ANODE RUBBER COMPANY, LTD. Fr. 643,762, Nov. 10, 1927. Added ingredients and stabilizing agents are added to latex before or during concn. by evapn., and accelerators and vulcanizing agents are added afterward. The stabilizing agents may include colloids such as glue, gelatin, casein, vegetable gums, dextrin or soap, Na_2SiO_3 or viscose. In an example ZnO 8, S 25, lampblack 1, talc 20, whiting

15, emulsified paraffin wax 2 and finely ground mineral rubber 1, are mixed with 100 parts of water contg. KOH 0.1, oleic acid 0.3 and casein 0.3 part. Preserved latex contg. 60 parts rubber is added and the whole mixed and concd. After concn. NH_3 and an accelerator such as 0.3 part diethylammonium diethyldithiocarbamate are added during cooling, the mixing being continued until both are uniformly distributed. Other examples are given, in one of which S and piperidine piperidylcarbothionolate are added during the latter part of the concn.

Rubber latex. RUBBER LATEX RESEARCH CORP. Fr. 644,605, Nov. 3, 1927. Latex is stabilized by adding blood or hemoglobin in quantity representing 5–25% of its content of rubber.

Concentrating latex. METALLBANK UND METALLURGISCHE GES. A.-G. (to K. D. P., Ltd.). Brit. 293,771, July 11, 1927. According to an example, there is added to fresh tapped latex 0.5% K salicylate or 0.25% KF and 0.25% KOH and the mixt. is inspissated. Other similar substances may be also used.

Treating latex. GENERAL RUBBER CO. Brit. 294,002, Aug. 25, 1927. Rubber latex is treated with a creaming agent such as NH_4 alginate and allowed to stand until it seps. into an uncoagulated rubber-contg. upper layer and a lower layer contg. sol. non-rubber constituents; the upper layer is then removed and the rubber is either used directly in manuf. or is spray dried or otherwise suitably treated. The latex may be subjected to 2 or more successive creaming treatments. Cf. *C. A.* **22,** 3551.

Rubber compositions. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 293,502, April 19, 1927. Viscous liquid or semi-solid accelerators, "anti-ageing" substances or softeners, *e. g.*, oleic acid, aldol-α-naphthalene or crotonaldehydeaniline are mixed with colophony before they are added to the rubber. Solvents may be used or the substances may be melted together.

Rolls for masticating or mixing rubber, etc. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 293,519, May 11, 1927. Direct water-cooling of the rolls is made more efficient by rust prevention, by placing wear-resisting material such as balls or cylinders of iron, stone, or rubber inside the rolls.

Forming rubber tubing on a fusible core. DUNLOP RUBBER CO., LTD., and A. W. T. HYDE. Brit. 293,535, May 26, 1927. An aq. rubber dispersion is deposited on a core or mandrel such as Wood's alloy (either electrophoretically or by dipping) and the core is removed by fusion. Various details and modifications are described.

Product for making tires puncture-proof. COLONIAL RUBBER. Belg. 347,420, Jan. 31, 1928. Rubber, glycerol or glucose in which is suspended powdered cork or vegetable fibers is mixed hot with a mineral pulverulent constituent such as talc, mica, or $MgCO_3$.

Product for making tires puncture-proof. G. L. HUYSMANS. Belg. 347,557, Jan. 31, 1928. The product consists of an aq. soln. of animal gelatin, glucose, glycerol and nitrobenzene, or similar products, contg. non-decomposable pulverulent or fibrous mineral matter.

Deposition of rubber. W. A. WILLIAMS. Brit. 293,815, April 8, 1927. See Fr. 638,630 (*C. A.* **23,** 547).

Rubber deposition by electrophoresis. DUNLOP RUBBER CO., LTD., and F. H. LANE. Brit. 293,343, April 6, 1927. In order to det. the c. d. necessary for the electrophoretic deposition of rubber of desired character, a test anode is used which is mounted so as to bear a varying c. d. along its length and therefore a deposit of varying character. A scale may indicate the c. d. at each point of the anode. Various structural and manipulative details are given.

Rubber sheets by electrodeposition. JOHN PORTER. U. S. 1,702,705, Feb. 19. Deposition from latex is effected on the surface of a bi-polar electrode of readily oxidizable metal such as Pb while at the same time oxidizing the metal and reducing the metallic oxide, as by electrolytic action. An app. is described.

Rubber floor-covering composition. CYRUS F. WILLARD. U. S. 1,702,678, Feb. 19. Vulcanized sheets are formed of a compn. comprising mixed rubber and fiber 65, S 3, thiocarbanilide 0.5, $Ca(OH)_2$ 2.5, petrolatum 4, Fe_2O_3 6, paraffin 2, and wood flour 17 parts.

Machine for reducing waste rubber to a fine powder. VICTOR D. LLOP. Fr. 644,296, Oct. 29, 1927.

Recovering cotton or other fiber from rubber fabrics. D. F. WILHELMI (to Naamlooze Vennootschap Vereenigde Nederlandsche Rubberfabrieken). Brit. 293,419, July 6, 1927. Material such as that of old tires, while it may be held by feed rolls and immersed in water or subjected to water jets or sprays, is combed or torn asunder and the liberated fibers are afterward sepd. from the water. Various details of operation and of the app. used are described.

Vulcanizing rubber. OSKAR FISCHER. Ger. 467,863, Dec. 9, 1925. The known method in which a mixt. of rubber with S and a mixt. of rubber with a vulcanization accelerator are mixed together prior to vulcanization is modified by mixing the mixts. continuously and in small amts. at a time.

Apparatus for repairing rubber articles by vulcanization. MAXIMIN MOMPIOU. Fr. 643,866, Nov. 15, 1927. The platform on which the article rests is indirectly heated by hot gases.

Treating rubber latex. I. G. FARBENIND. A.-G. Brit. 294,804, Oct. 10, 1927. A viscous paste which can be readily redispersed by use of aq. NH_3 is prepd. by quickly mixing with latex sufficient acid to give a p_H less than 2 and then (suitably after about 24 hrs.) filtering off the serum. Fillers, protective colloids, S, etc., also may be added.

Treating latex. I. G. FARBENDIND. A.-G. Brit. 294,412, Nov. 12, 1927. Latex is preserved by the addn. of small quantities (suitably 2–5%) of sol. salts of sulfonic acids possessing soap-like properties. The addn. improves the penetration when the latex is used for impregnating paper or other materials and the materials in such processes may also be treated with salts such as are admixed with the latex. Several examples are given.

Variegated rubber. C. MACINTOSH & Co., LTD., and S. A. BRAZIER. Brit. 295,080, May 21, 1927. Pieces of rubber of the same or different colors are coated with a rubber soln. of a contrasting color, dried and agglomerated into a mass which has a variegated surface.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 294,661, July 28, 1927. Polymerization of hydrocarbons such as butadiene, isoprene, dimethylbutadiene or their analogs by means of O or a substance yielding O, or both, in an aq. medium as described in Brit. 283,840 (*C. A.* **22**, 4274), is effected in the presence of a metal salt of an inorg. or org. acid such as salts of Co, Pb, Mn, Cr, Ni, or Ag. Several examples are given. Cf. *C. A.* **23**, 310.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 294,963, Aug. 2, 1927. Polymerization of butadiene, isoprene, or similar hydrocarbons is effected in the presence of water by a substance which exerts a hydrotropic action, such as a salt of an org. sulfonic or carboxylic acid or a substitution product of such an acid or an acid obtained from the degradation of albumin or an acid amide. The substance can either be added as such or can be produced *in situ* by adding an alkali, metal oxide or metal carbonate or acid of suitable character. O or O carriers may be present during the process. Examples are given of the treatment of isoprene and butadiene with water at a temp. of about 60° in the presence of casein and K cinnamate, blood albumin and Na tetrahydronaphthalene sulfonate, Mg isobutylnaphthalene sulfonate and O, and egg albumin and Na stearate.

Rubber-like substance from mineral oils. EDGAR W. HULTMAN (one-fourth each to Francis P. Dunckiee, Joseph Monteleone, and Walter R. Simons). U. S. 1,704,194, March 5. A mineral oil material such as "Dubbs pressure distillate," topped Calif. crude oil or other similar oil or fraction, substantially free from constituents b. below 200°, is partially polymerized (suitably by use of oxides of Ce or Sn at a temp. of about 95°), then cooled and treated with an activated reducing gas such as CO or CH_4 in the presence of Ni, Pd, or other catalyst at a temp. below that used in the polymerizing reaction (suitably at a temp. of about 32°), treated with a halogenating reagent such as Cl, Br, or B fluoride, to produce a soft rubbery product in the resulting oily material, and sepn. is then effected.

Preserving rubber articles. A. FORNER. Brit. 294,632, July 29, 1927. The surface of articles such as tires is treated with a mixt. of French chalk and a gum soln. with or without a soln. of "cellulose." The mixt. may be thinned with "benzole or benzene."

Molding hollow rubber balls. K. KUROKAWA. Brit. 295,175, Dec. 19, 1927. An app. is described.

Core for single-tube tires. SCHUYLER C. HATFIELD. U. S. 1,704,538, March 5. Cores are formed with a filling of comminuted material such as sand surrounded by a thin casing of sol. material such as glue, shellac, or rosin which can readily be removed from the tube by washing.

Traveling band filter suitable for filtration of aqueous rubber dispersions. A. SZEGVARI and C. M. SPENCER (to Anode Rubber Co., Ltd.). Brit. 294,215, July 20, 1927. Metal parts of the app. are preferably made of stainless steel and various structural features are described.

Rubber solution for coating wood, metal, or other materials. CHARLES E. BRADLEY and WILLIS A. GIBBONS (to Naugatuck Chemical Co.). U. S. 1,703,920, March 5.

Halogenated rubber treated with S chloride is dissolved in benzene and solvent naphtha. Boiled linseed oil, etc., may be added.

Apparatus for coating, impregnating, or electrophoretic deposition of rubber. A. SZEGVARI (to Anode Rubber Co., Ltd.). Brit. 294,153, July 18, 1927. An app. is described in which the homogeneity of an aq. dispersion such as rubber is maintained by circulating the dispersion through a tank or chamber in a continuous stream and filtering it during circulation to remove particles above a certain desired size.

Deposition of rubber. THE ANODE RUBBER CO., LTD. Fr. 645,779, Dec. 15, 1927. Org. material, particularly rubber, is deposited electrophoretically on supports which are cooled below the temp. of the bath so as to remove the heat caused by the current, or sep. cooling means may be employed.

Composite rubber flooring manufacture. JOHN B. LOSEY and WALTER R. STONE. U. S. 1,703,312, Feb. 26. Mech. features.

Adhesive. MARY A. F. ALLEN. Australian 10,707, Dec. 3, 1927. An adhesive consists of 2 co-acting fluids, the first rubber latex or rubber emulsion and the second a soln. of raw or unvulcanized rubber in CCl_4 or C_6H_6. Na_2SiO_3 may be added to the latex to reduce its viscosity.

Polymerized vinyl compounds of rubber-like character. I. G. FARBENIND. A.-G. Brit. 294,474, July 23, 1927. Polymerization of substances such as vinyl esters or ethers is effected in the presence of substances imparting improved elasticity to the product such as proteids or their degradation products such as peptones, peptides, diketopiperazines and amino acids and other N compds. preferably of high mol wt. Examples are given of the use of casein with vinyl acetate, albumin with vinyl acetate, glycocoll with vinyl acetate and naphthalene with vinyl acetate. The products may be vulcanized, with or without accelerators, fillers, and plastifiers.

Vulcanizing rubber. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,703,902, March 5. Vulcanization with S is accelerated by use of a reaction product of diphenylguanidine with 1-keto-2-methyl-4-thio-3,5-benzenedithiol. Cf. *C. A.* **23**, 732.

Apparatus for vulcanizing small objects such as dental plates. MAXIME PAULMIER. Fr. 644,748, Nov. 30, 1927.

Treating rubber latex. P. MEYERSBERG. Brit. 295,660, Aug. 16, 1927. Natural or artificial latex is partially coagulated and rendered suitable for use in coating fabrics by adding weak org. acids such as rosin, elaine, stearic acid or linseed-oil acid, which react with the alkali which is present or which is added to form soaps. Fillers and disinfectants also may be added and if rosin is used it may be dissolved in colza or other suitable oil.

Improving the electric insulating properties of rubber products obtained directly from latex. K. D. P., LTD. Brit. 296,032, Aug. 23, 1927. The serum constituents are removed from latex, *e. g.*, by dialysis, by the method described in German pat. No. 412,060, or by treating the latex with agglutinating agents as described in German pat. No. 442,856 and centrifuging.

Working up rubber. L. SZYNKOWSKI. Ger. 471,496, June 2, 1927. Crude natural rubber is cut up, given a short drying, and caused to swell by treatment with suitable hydrocarbons. The mass is then kneaded, filtered, and worked up as usual.

Rubber compositions. ERNEST R. BRIDGWATER and AARON S. SLACK (to E. I. du Pont de Nemours & Co.). U. S. 1,705,712, March 19. In order to control the tendency of rubber to "scorch" or prematurely vulcanize during the necessary operations preceding vulcanization (such as dispersion of compounding ingredients with the rubber) and to improve the tensile strength and other properties of the rubber, it is incorporated with a small proportion (suitably about 1–3%) of the reaction product of diphenyldiaminomethane with stearic acid (or other suitable compd. formed by condensing 2 mol. proportions of a primary aromatic amine with 1 mol. proportion of an aliphatic aldehyde and treating the resulting diamine with a high aliphatic acid).

Thermoplastic rubber derivative. WILLIAM C. GEER and HERBERT A. WINKELMANN (to B. F. Goodrich Co.). U. S. 1,705,757, March 19. Rubber is incorporated with a softener such as pine tar and with concd. H_2SO_4 or other suitable isomerizing agent, and the mixt. is heated (suitably at a temp. of about 130° or higher) until it has assumed an inelastic thermoplastic condition and is then masticated to homogenize it.

Transformation products of rubber. THE B. F. GOODRICH CO. Fr. 646,414, Dec. 27, 1927. Conversion products of rubber are obtained by heating it with a phenol and one of the following: chlorinated rubber, rubber-HCl, rubber sulfur chloride, chlorinated rubber-HCl, pinene-HCl, diphenylamine-HCl, trichloroaniline-HCl, *m*-nitraniline-HCl, $HgCl_2$, $SnCl_4$, naphthalene tetrachloride, triphenylchloromethane,

$ZnBr_2$, rubber dibromide, diphenylamine-HBr, $CaSO_4$, $Al_2(SO_4)_3$, $HgSO_4$, diphenylamine sulfate, diphenylamine trichloroacetate. Phenols include cresol, PhOH, catechol, resorcinol naphthols and *p*-chlorophenol. Several examples are given in which the temp. is kept at 134–160° for 20 hrs. or longer.

Apparatus with an abrading drum for grinding or comminuting rubber. C. E. GARDNER. Brit. 295,434–5, May 12, 1927. Structural features.

Dipped rubber articles. E. HAZELL (to Naugatuck Chemical Co.). Brit. 295,700, Aug. 19, 1927. Deposition of rubber from latex on porous molds is accelerated by (1) diln., (2) addn. of substances increasing the rate of filtration of the aq. portion of the material through the deposit as it forms, (3) agitation, or (4) heating. For increasing the filterability, ZnO or a Zn salt and a sulfide such as that of Na, K, Li, or NH_4 may be added. Various details of procedure are given.

Rubber articles from aqueous dispersions. P. KLEIN (to Anode Rubber Co., Ltd.). Brit. 296,107, Feb. 23, 1927. Rubber from aq. dispersions such as those formed from reclaimed or waste rubber is deposited by a continuous building-up process, upon a backing from which the product may be stripped either before or after subjection to vulcanization. The process may involve electrophoresis, suction or chemical action, and various details and modifications are described.

Forming vehicle bodies and associated parts of pliable "semi-hardened" rubber. A. LEVY-PICARD. Brit. 295,541, Dec. 21, 1927.

Synthetic rubber. I. G. FARBENIND. A.-G. Fr. 646,704, Jan. 4, 1928. Products of the nature of rubber latex are obtained by emulsifying butadiene, its homologs or analogs in water with the aid of emulsifying agents and polymerizing these emulsions with the addn. of buffers such as establish a p_H value of 4 to 8.5. In examples, isoprene is emulsified with the addn. of NH_4 oleate and Na phosphates or Na oleate and Na isobutylnaphthalenesulfonate, or Turkey-red oil and Na_3PO_4, and heated for 2 or 3 weeks. The latex formed is coagulated by the addn. of AcOH, HCl, etc. Cf. *C. A.* **23,** 2071.

Vulcanizing rubber. MORRIS L. WEISS (to Dovan Chemical Co.). U. S. 1,705,948, March 19. Vulcanization is accelerated by use of a suitable substituted guanidine having 2 substituting aryl groups (at least one of the aryl groups being unsubstituted). Cf. *C. A.* **22,** 1061.

Vulcanizing rubber boots. L. E. DE SANKTI-MAURO-GAEVSKII. Russ. 4798, Mar. 31, 1928. The usual vulcanization is carried out in an atm. of flue gases.

Vulcanization apparatus. THE AKRON STANDARD MOLD CO. Fr. 646,003, Dec. 13, 1927.

Rubber. ELBERHARD MEYER-BURSCH. Ger. 471,879, July 6, 1924. Addn. to Ger. 463,290. Artificial objects are prepd. by impregnating tissues, textiles, paper, pasteboard, wood and leather with rubber and esters of tetrahydronaphthols, with or without simultaneous treatment with a volatile solvent. Filling material is subsequently added.

Rubber. THE ANODE RUBBER CO. (England), LTD. Fr. 467,413, Jan. 17, 1928. In the treatment of natural latex to produce rubber objects, an artificial dispersion of rubber is added to the latex before coagulation. The rubber may be mastic or nonmastic or a mixt. of both. The compn. of the dispersion may be modified by adding during the formation of the deposit a dispersion contg. more or less mastic rubber than the initial dispersion. Cf. *C. A.* **23,** 1777.

Rubber. SOC. ANON. DES CHARBONS ACTIFS EDOUARD URBAIN. Fr. 647,151, June 1, 1927. Absorbent substances, preferably active C, finely ground to a quasi-colloidal state and dried, are used as "charges" in the manuf. of rubber.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 647,041, Jan. 13, 1928. Artificial rubber is prepd. by emulsifying butadiene, isoprene, dimethylbutadiene, etc., alone or mixed together with aq. liquids or viscous liquids contg. water and emulsifying agents, in the presence of O or agents liberating O. In examples, isoprene and dimethylbutadiene are emulsified with egg albumin, Marseilles soap and water, polymerization taking place on heating in the presence of O. Isoprene and alkali oleate are emulsified in water with Na perborate and polymerized at 60–70°; they are stirred in the presence of air. Isoprene and butadiene are dissolved in Na isobutylnaphthalenesulfonate and polymerized in the presence of K percarbonate at a moderate temp. Fr. 647,042 describes a process in which the above hydrocarbons are polymerized by means of org. hydroxylic compds. with or without the addn. of inorg. hydroxylic compds. and indifferent solvents. In an example, isoprene, glycerol and Na are stirred at 60° in CO_2, a clear yellow product being obtained. The glycerol may be replaced by starch, ethyl cellulose, or isoprenic alc.

Synthetic rubber. R. P. DINSMORE (to Goodyear Tire & Rubber Co.). Brit.

297,050, Sept. 13, 1927. In effecting polymerization of rubber-forming hydrocarbons such as isoprene or dimethyl butadiene, the hydrocarbons are treated with an emulsifying agent such as NH_4 oleate or K oleate, and with a protective colloid such as a protein, *e. g.*, casein or egg albumin. A product of improved quality is stated to be obtained, presumably due to the production of an emulsion of the hydrocarbon, the minute globules of which are subsequently polymerized.

Deposition of rubber, etc. THE ANODE RUBBER CO. (England), LTD. Fr. 647,232, Jan. 16, 1928. Layers of org. substances, particularly rubber, obtained by deposition from aq. dispersions, are dried throughout by keeping a higher temp. on the side opposite to that at which moisture is evapd. than on the latter side. Moist air may be circulated on the side at which drying is retarded. If the drying takes place on metallic molds, the molds are heated, if on porous molds, the surrounding air is heated.

Rubber electrodeposition. P. KLEIN (to Anode Rubber Co., Ltd.). Brit. 296,138, March 16, 1927. The uniformity of thickness of the deposits is influenced by screens which may be formed of insulating material such as hard rubber or celluloid or may be conductive to form equi-potential surfaces. If sep. anode and cathode chambers are used, the screens are preferably placed in the cathode chamber. Cf. *C. A.* **23**, 2067.

Preserving rubber. A. M. CLIFFORD (to Goodyear Tire & Rubber Co.). Brit. 296,398, Aug. 31, 1927. There is added to rubber a reaction product of a diamine and a naphthalene deriv., such as the compd. prepd. by mixing mol. proportions of β-naphthol and ethylenediamine with one-half mol. anhyd. $CaCl_2$ and heating for 5–8 hrs. at 270°, or the reaction product of a naphthol and phenylenediamine.

Preservation of rubber. THE GOODYEAR TIRE & RUBBER CO. Fr. 647,285, Nov. 29, 1927. Rubber is preserved by incorporating in the mixt. to be vulcanized the reaction product of a phenol and an amine. Suitable compds. include phenyl-β (or α)-naphthylamine and diaminodiphenyl-β-naphthylmethane (by reacting β-naphthol with CH_2O to form methylene-di-β-naphthol, which is heated to 280° with $PhNH_2$ in the presence of $CaCl_2$). Cf. preceding abstract.

Rubber dispersions. P. KLEIN and A. SZEGVARI (to Anode Rubber Co., Ltd.). Brit. 296,685, March 4, 1927. Aq. dispersions of substances such as vulcanized or unvulcanized rubber, rubber waste, reclaimed rubber, rubber substitute, synthetic resins, balata or gutta percha, or mixts. of such substances are prepd. by bringing the material into a plastic condition by mech. treatment and then successively adding 2 reagents which react to form a dispersing substance, such as oleic acid and NH_3. Various compounding substances may be added to the plastic material before dispersion.

Apparatus for maintaining rubber dispersions in circulation to keep them in uniform condition. P. KLEIN, S. GOTLEB, A. SZEGVARI and G. F. WILSON (to Anode Rubber Co., Ltd.). Brit. 296,454, March 3, 1927.

Compounding "conditioning substances" with rubber dispersions. PAUL KLEIN and ANDREW SZEGVARI (to Anode Rubber Co., Ltd.). U. S. 1,708,181, April 9. A rubber dispersion is treated with "conditioning substances" in the form of a dispersion, the particles of which consist of a combination of 2 or more different substances, such as S and vulcanized oil.

Uniting different pieces of rubber. P. KLEIN, F. GABOR and A. SZEGVARI (to Anode Rubber Co., Ltd.). Brit. 297,127, March 16, 1927. Two or more pieces (such as those for making hollow rubber articles) formed from natural or artificial rubber dispersions by electrophoresis, dipping, spreading, spraying, or impregnating, are brought into contact with each other in a moist or incompletely dried or coagulated condition; union is effected by further drying or coagulation.

Use of rubber to join parts of shoes, etc. FRESKO TEKNISK-KEMISK FABRIK AKTIESELSKAB (to J. W. Radburne). Brit. 296,372, Aug. 30, 1927. In joining soles and uppers or other parts of shoes the surfaces to be joined are roughened, treated with rubber or latex solns. contg. vulcanizing substances and, when these coatings are dry, further treated with rubber soln. contg. an accelerator, and pressed together.

Apparatus for forming wide rubber strips by extrusion. L. WETMORE (to Goodyear Tire & Rubber Co.). Brit. 296,976, Sept. 10, 1927. Structural features.

Utilizing waste rubber. COGEDEX COMPAGNIE GÉNÉRALE D'EXPLOITATION SOC. ANON. Brit. 296,395, Aug. 31, 1927. See Fr. 640,332 (*C. A.* **23**, 1013).

Grinding fibrous rubber scrap or similar material. HERBERT G. DAY (to Philadelphia Rubber Works Co.). U. S. 1,708,123, April 9. The material is passed through a high-speed mill in the presence of steam at such low pressure as to avoid any substantial wetting of the material. An app. is described.

Rubber articles. THE ANODE RUBBER CO. (England), LTD. Fr. 648,037, Jan. 31, 1928. In the production of articles by repeated dipping of a mold into org. dispersions, particularly of rubber, the mold is heated between the dippings and, if desired,

during dipping. Between the dippings the mold should be kept moist. Means for promoting coagulation, such as gypsum molds or porous molds through which the moisture is drawn, may be used.

Flower pots, vases, etc., made of rubber. C. PAPWORTH and E. JARVIS. Brit. 296,583, Oct. 20, 1927. Various structural details as to reinforcing the rubber, etc., are described.

Rubber vulcanization accelerators. L. B SEBRELL (to Goodyear Tire & Rubber Co.) Brit. 297,051, Sept. 13, 1927. An accelerator is made by reaction of a mercaptothiazole with an aldehyde amine condensation product, *e. g.*, mol. proportions of mercaptobenzothiazole and crotonaldehyde aniline reaction product are mixed and refluxed for 2 hrs. or longer. Other reagents which may be used include: mercaptonaphthothiazoles, mercaptomethylthiazoles and reaction products of acetaldehyde and aniline, crotonaldehyde and methylamine, propylaldehyde and ethylamine, butylaldehyde and aniline, butylaldehyde and toluidine, heptaldehyde and aniline, heptaldehyde and butylamine and cinnamic aldehyde and aniline.

Rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 648,631, Feb. 10, 1928. Aq. dispersion of org. substances, particularly vulcanized or unvulcanized or regenerated rubber or factis, is obtained by mixing the solid constituent after mastication successively with at least 2 auxiliary substances, at least one of which presents to the solid constituent and at least one to the liquid constituent a high physical affinity (soly., miscibility, swelling capacity, and adsorption capacity) and at least one of the substances added first combining chemically with one of the substances added afterward under the conditions of working. Thus, regenerated rubber is treated in mixing cylinders, NaOH lye is added and afterward olein. Water contg. NH_3 is added until reversion, and the dispersion of rubber obtained may be dild. as desired, preferably with feebly alk. water. Casein may be added with the NaOH.

Rubber. SOC. ANON DES CHARBONS ACTIFS ÉDOUARD URBAIN. Fr. 648,194, June 14, 1927. A charge is used in the making of rubber consisting of an active or activated porous absorbent substance, which has absorbed vulcanizing substances. In examples, C, having served for the purification of coal gas and contg. 6–7% of S, thiols, thiophene, different amines and cyanides, is ground and dried and mixed with rubber and vulcanized. C used for coal-gas purification is caused to absorb vapors of piperidine and CS_2 and used as before. Cf. *C. A.* **23**, 2603.

Rubber. SYNDICAT FRANCO-NÉERLANDAIS. Fr. 649,006, July 4, 1927. Waste vulcanized rubber, contg. no charge, after removal or destruction of any fabric, is regenerated by treating it with latex, giving a rubber equal to plantation rubber. Fr. 649,007 describes the coagulation of latex by means of waste vulcanized rubber, contg. no charge, and after removal or destruction of any fabric.

Rubber composition. HARRY H. KELLER. U. S. 1,710,481, April 23. A vulcanizable compn. which is suitable for tire treads, floor coverings, shoe soles, etc., is formed of rubber 100, S 3, ZnO 26.5 and Al oxide 26 parts and an accelerator.

Liquefied rubber composition. HAROLD P. BUTLER. U. S. 1,710,470, April 23. In prepg. a product which may be used with a brush or as a spray, rubber is placed in a still together with C_6H_6, toluene, or CCl_4 and refluxed for several hrs. Cf. *C. A.* **22**, 2291.

Rubber deposition from latex. P. KLEIN, A. SZEGVARI, R. F. MCKAY, C. HAYES and G. W. TROBRIDGE. Brit. 298,117, March 26, 1927. The properties of rubber produced by direct deposition from aq. dispersion are improved by submitting the surfaces not in contact with the deposition strata to the action of coagulating agents before drying. The treatment may take place alternately with the deposition of layers and coagulation may be effected by the application of a heated liquid such as hot water, hot moist air, steam, liquid coagulants such as HOAc or $CaCl_2$ soln. or coagulating vapors.

Electrophoretic deposition of rubber. P. KLEIN, A. SZEGVARI, R. F. MCKAY, C. HAYES and G. W. TROBRIDGE. Brit. 297,780, March 26, 1927. In the deposition of rubber from dispersions contg. insufficient OH ions to cause gas formation on the anode, as described in Brit. 257,885 (*C. A.* **21**, 3141), the cond. of the dispersion is altered by the addn. of electrolytes free from OH ions or by removing electrolytes from the dispersion and replacing them by electrolytes free from OH ions. This treatment enables the OH concn. to be increased above the limit otherwise possible without gas formation. In using Zn anodes, alkali metal chlorides serve to prevent sticking of the rubber at the anodes and to produce softer deposits. $CaCl_2$ increases coagulation and substances such as an alkali metal ferrocyanide or phosphates increase the toughness of the deposits.

Coloring rubber. I. G. FARBENIND. A.-G. Brit. 298,364, Oct. 6, 1927. Rubber is colored orange-red by mixing it, before vulcanization, with the Ca salt of benzeneazo-2-hydroxynaphthalene-6-sulfonic acid (Schultz No. 37).

Forming rubber articles by dipping. DUNLOP RUBBER CO., LTD., and D. F. TWISS. Brit. 297,911, July 25, 1927. A non-porous mold such as one of glazed porcelain, metal, or rubber is moistened with a coagulant liquid such as $CaCl_2$, K alum, or formic or acetic acid soln. and dipped in a concd. dispersion, which may contain fillers and vulcanizing ingredients and which may include "mineral rubber" and reclaimed rubber and a salt such as NaCl, Na_2SO_4, or $CaSO_4$.

Rubber-filament formation by extrusion. M. DRAEMANN. Brit. 297,912, July 25, 1927. Filaments are formed from a soln. of unmasticated rubber, which is maintained at a temp. above the b. p. of the solvent used. The filaments after formation are carried by a belt conveyor through a chamber where they are vulcanized by molten S or hot air, and, before, during, or after vulcanization, the filaments may be stuck together to form a band by use of liquid S, glue, casein, or other suitable material. App. and various other details of procedure also are described.

Molding rubber tires. W. J. FIELDHOUSE. Brit. 297,590, Nov. 9, 1927. The outer covering of a cushion tire is molded over the core portion by an extrusion process. An app. is described.

Molding inner tire tubes or other hollow rubber articles. T. L. FAWICK. Brit. 298,139, Oct. 3, 1927. Mech. features. Brit. 298,140 describes a special form of tire vulcanizing app.

Forming endless circular rubber inner tire tubes for vulcanization. OTTO J. KUHLKE (to Kuhlke Machine Co.). U. S. 1,709,796, April 16. Mech. features.

Forming "punctureproof" tire tubes by conjoint use of slow curing and fast curing rubber compositions. OTTO J. KUHLKE. U. S. 1,709,797, April 16. Various mech. details are described.

Progressive refrigeration of rubber strips to facilitate cutting. JOHN R. GAMMETER (to A. G. Spalding and Bros.). U. S. 1,710,211, April 23. An app. is described.

Reclaiming rubber. JOHN J. MORIARTY (30% to James H. S. Kerr). U. S. 1,710,100, April 23. Fiberized and vulcanized material is ground, incorporated with a plasticizing material such as "mineral rubber;" the material is milled with the further addn. of a reclaiming reagent such as a 20% H_2SO_4 soln. and is then treated with steam under pressure.

Forming and vulcanizing cored rubberized belting. JOHN R. GAMMETER (to B. F. Goodrich Co.). U. S. 1,709,209, April 16. Mech. features.

Vulcanizing rubber. W. C. GEER, B. DALES and B. F. GOODRICH CO. (to Anode Rubber Co., Ltd.). Brit. 297,850, March 28, 1927. In the direct production of rubber goods on deposition strata or molds by dipping or electrophoresis, "ultra-accelerators" are used, which effect complete vulcanization of the products during or before completion of drying, and at temps. below 112° or even below the b. p. of water. Suitable substances are diethylaminediethyldithiocarbamate, dithiofuroic (dithiopyromucic) acid and dithiofuroates and mercaptobenzothiazole. The vulcanization may be effected in heated air, heated moist air, or by dipping in hot water. Various natural or artificial rubber dispersions and compns. may be used.

Vulcanizing rubber. W. SCOTT (to Rubber Service Laboratories Co.). Brit. 297,726, Sept. 26, 1927. A vulcanizing accelerator is made by treating an aldehyde-NH_3 with a further quantity of the same or a different aldehyde, preferably by heating in a closed vessel to 90–95°. Examples are given of the use of the reaction products of various proportions of butylaldehyde and butylaldehyde-ammonia, butylaldehyde and croton aldehyde-ammonia and croton aldehyde and butylaldehyde-ammonia.

Vulcanization of rubber. THE RUBBER SERVICE LABORATORIES CO. Fr. 648,239, Oct. 8, 1926. Accelerators for the vulcanization of rubber are obtained by reacting a mercaptan or compd. of mercaptan contg. a —CSH group on a completely saturated org. base. The products obtained may be condensed with an aldehyde such as crotonic aldehyde. Suitable bases include hexamethylenetetramine, biguanide, triphenyl biguanide, guanyl ureas, isoureas, thioureas, piperazine, trimethylsulfonium hydroxide and $N(CH_3)_4OH$. Mercaptan compds. include ethylmercaptan, thiophenol, thiocresol, mercaptobenzothiazoles, 2-mercaptothiazoline and its derivs., thioanilides, 2-mercaptobenzimidazole, mercaptoiminazole, thioamides, and thioammeline. Cf. *C. A.* **23**, 732.

Vulcanizing apparatus for pneumatic tubes. GILLETTE RUBBER CO. Fr. 648,504, Feb. 7, 1928.

Devulcanizing rubber. R. R. GROSS (to Firestone Tyre & Rubber Co. (1922), Ltd.). Brit. 297,817, Sept. 29, 1927. Rubber scrap such as that contg. textile reënforcements is treated with steam under a pressure of 400–1000 lbs. per sq. in. for 1–15 mins.; the pressure is then suddenly released; the scrap is thus disintegrated, the textile material is charred or hydrolyzed and free S is stated to be removed.

[Reprinted from THE RUBBER AGE (N. Y.),
Vol. 25, Nos. 2-3, April 25, and May 10, 1929]

The Oxidation of Vulcanized Rubber*

A. Van Rossem and P. Dekker

SINCE Kirchhof[1] in June, 1927, gave to the first general meeting of the German Rubber Society in Essen a detailed review of work concerned with the oxidation of rubber, it seems superfluous to publish any extensive bibliography thereon. We prefer to limit ourselves, for the present, almost exclusively to a few experiments in this field. However, we may refer in a general way to the work of others.

It is a notable fact that all investigations of the oxidation of vulcanized rubber have been always based on the kinetics of the oxygen combination, and, as far as isolation of the oxidation products is concerned, on a late stage of oxidation, the isolation of oxidation products during the early stages of oxidation being left out of consideration.

Thus, for example, Kirchhof[2] in his work published in 1913 studied the behavior of ground vulcanized rubber which had been heated for 100 hours in a current of air at 100° C. and thereby strongly oxidized, as indicated by the increase in weight (11-13%).

Eaton and Day[3] later in 1919 made experiments of a similar nature. Here, too, the kinetics principally were studied, and the samples were examined only after oxidation was far advanced. Again in Kirchhof's recent work already mentioned, the oxidation products were studied only after prolonged oxidation.

Although, from a purely scientific standpoint, an examination of badly oxidized rubber is thoroughly defensible, yet, on the other hand, it may be rightly said that the further oxidation has progressed, the more complicated becomes the mixture of decomposition products and the smaller the hope of explaining the mechanism of oxidation. From a technical standpoint the analysis of oxidation products at a rather late stage of oxidation appears aimless. If

*Translated from Kautschuk, Vol. 5, No. 1, pages 13-21, January, 1929, by J. P. Fahy.

one can perceive by appearance and smell that the rubber is oxidized, then it has long since lost its interest for industry.

What does interest the manufacturer of rubber articles, the rubber chemist, the tradesman, and the consumer especially are questions concerning the initial stage of oxidation, as for example: Has the rubber reached the first stage of oxidation, or perhaps what is more important, how can one determine whether the rubber will soon begin to oxidize.

From the work of Marzetti[4] we know that the aging of rubber and the associated changes in mechanical properties, which are of the greatest importance in manufacture, are due for the most part to an oxidation process, which at first is very small, not exceeding one per cent increase in weight, but which nevertheless has a very important effect on the mechanical properties.

Now there is one phase of rubber research which especially has to do with the changes in physical properties during the initial stages of oxidation, namely, the Geer-Evans accelerated aging test or the Bierer-Davis bomb test, which is rapidly becoming popular. However, we do not intend just now to follow the oxidation of rubber in its initial stages by means of these more mechanical tests; as we have said we wish to consider the oxidation of vulcanized rubber from the chemical analytical side. Hence we shall devote our attention especially to the importance of the alcoholic potash extract of vulcanized rubber.

Preliminary Examination of the Alcoholic Potash Extract of Vulcanized Rubber

It has long been known that the alcoholic potash extract after previous extraction with acetone affords a method for determining the quantity of factice in simple rubber compounds. It is also known that in the presence of mineral rubber, asphalt, etc., the method is very unreliable, as these substances unless previously extracted with chloroform are found in part in the alcoholic potash extract. Finally it was known that in the case of oxidized rubber articles a portion of the oxidation products is soluble in alcoholic potash and therefore is included in the extract on analysis.[5]

It seemed advisable to proceed systematically and obtain some insight into the relationship between the amount of alcoholic potash extract and the degree of oxidation at various stages of vulcanization. For this purpose the simplest possible mixture was chosen, namely, 92.5 parts rubber and 7.5 parts sulfur. This compound was given a series of cures in an autoclave at 3.5 atmospheres or 147° C. The finely ground samples were analyzed and aged in open dishes in diffused light. After 1 and 2 weeks, and 2, 4, 8, 12, and 18 months the analyses were repeated.

The following determinations were made:

a. **Acetone extract,**
b. **Free sulfur,**
c. **Combined sulfur,**
d. **Alcoholic-potash extract.**

At the time these experiments were begun, that is, about six years ago, the potash extract determination was made in the following way: 2 g. of rubber previously extracted with acetone were covered with 20 cc. of benzene and allowed to swell over night. The next day it was heated with 40 cc. of 0.5*N* alcoholic potash for

four hours on the steam bath under a reflux condenser, filtered, and washed a few times with boiling alcohol and water. The filtrate together with the wash water was evaporated almost to dryness (3 to 5 cc.) The residue was taken up in about 100 cc. of water, and after acidifying with hydrochloric acid was shaken up with ether in a separatory funnel. The ether extract was evaporated and dried at 100° C. to constant weight.

e. Preliminary qualitative examination of oxidation products in the alcoholic potash extract.

The alcoholic potash extract consists of some possible oxidation products of the rubber and also some fatty acids, obtained from esters insoluble in acetone which are saponified by the alcoholic potash and which on subsequent acidification are found in the ether extract as fatty acids, as shown by the authors in 1926.[6] Dekker noticed in an analysis of rubber insulation containing factice that a more or less coherent film, consisting apparently of oxidation products of the rubber, remained behind if the alcoholic potash extract was heated after drying with more alcoholic potash, whereupon the factice acids dissolved, passing over to soluble soaps. The extract was therefore heated with 20 cc. of O.5*N* alcoholic potash for one hour on the steam bath under a reflux condenser, and then the liquid was poured off. At first the quantity of insoluble constituents remaining behind was judged only qualitatively.

f. Aqueous extract.

The aqueous extract was also determined because Eaton and Day[7] have noticed that vulcanized rubber when badly oxidized has a considerable quantity of aqueous extract.

From the mass of experimental data we have taken two series of experiments (Table I), which are based on vulcanized rubber containing 4.2% and 5.9% combined sulfur.

From these figures the important fact is evident that the alco-

Table I

CHEMICAL CHANGES OF VULCANIZED RUBBER ON AGING

Time	Increase in weight	Organic acetone extract	Alcoholic potash extract	Oxidation products	Aqueous extract
4.2% combined sulfur					
Before aging	.....	3.0%	0.8%	.....	0.2%
After 1 week	0.08%	3.0%	0.8%	x	0.2%
" 2 weeks	0.10%	2.8%	0.9%	x	0.2%
" 1 month	0.13%	2.8%	1.0%	x	0.2%
" 2 months	0.13%	2.9%	1.0%	x	0.3%
" 4 "	0.42%	2.8%	1.4%	xx	0.2%
" 8 "	0.50%	2.9%	2.8%	xxx	0.2%
" 12 "	0.70%	3.7%	2.4%?	xxx	0.3%
" 18 "	1.60%	4.7%	5.2%	xxxx	0.6%
5.9% combined sulfur					
Before aging	.....	2.7%	1.3%	.....	0.2%
After 1 week	0.07%	2.6%	1.5%	x	0.2%
" 2 weeks	0.13%	2.6%	1.7%	xx	0.2%
" 1 month	0.27%	2.5%	1.5%		0.2%
" 2 months	0.42%	2.8%	3.4%	xxx	0.3%
" 4 "	2.1%	5.6%	7.6%	xxxx	0.4%
" 8 "	17.6%	31.6%	9.2%	xxxx	5.9%
" 12 "	20.3%	44.4%	*		12.5%
" 18 "	24.5%	42.8%	*		17.0%

*The alcoholic potash extract cannot be determined because of the large amount insoluble in ether.

holic potash extract during the initial stages of oxidation is a much more sensitive quantitative measure of oxidation than the other values. The organic acetone extract at first remains absolutely constant, while the alcoholic potash extract increases slowly but much faster than the increase in weight due to absorption of oxygen. In the case of a combined sulfur content of 4.2%, the aqueous extract increases only after 18 months, while in the case of 5.9% combined sulfur a considerable quantity of aqueous extract is obtained but only when the acetone extract itself has greatly increased. In these series the oxidation products in the alcoholic potash extract are given only approximately as 1 to 4 x. However, an increase in the quantity is evident.

As the oxidation becomes more advanced, a portion of the alcoholic potash extract becomes insoluble in ether after acidification, so that the quantitative determination of the alcoholic potash extract no longer has any value.

Procedure

In continuing this work the oxidation products were determined quantitatively. After heating the alcoholic potash extract with 20 cc. of O.5*N* alcoholic potash, the insoluble products, which for the most part clung as a film to the bottom of the flask, were washed into a Gooch crucible and dried at 100° C. to constant weight. If the film stuck to the bottom of the flask, it was allowed to stand for some time under water or warmed for a short time on the steam bath. The film then separated quantitatively from the bottom of the flask and could be transferred to a Gooch crucible.

Experiments were now begun to determine the influence of the method on the quantitative estimation of the alcoholic potash extract and the oxidation products. A compound of 92.5 parts rubber and 7.5 parts sulfur was given a series of cures and allowed to age naturally for six months. After this period the determination of the alcoholic potash extract and the oxidation products was carried out according to various methods.

Table II contains the experimental data for three methods A, B, and C.

These results show that:

1. Previous swelling in benzene is quite essential.
2. The most favorable benzene-alcohol ratio is not 20:40 but 50:50.

Further experimental data show:

Table II

INFLUENCE OF THE METHOD OF ANALYSIS ON THE QUANTITATIVE DETERMINATION OF THE ALCOHOLIC POTASH EXTRACT AND OXIDATION PRODUCTS.

Compound: Rubber 92.5 parts
Sulfur 7.5 parts

Vulcanized with increasing time of cure and aged six months.

			Combined sulfur			
			1.8%	4.3%	6.0%	7.0%
A)	No swelling in benzene, 2 g. rubber+40 cc. O.5*N* alcoholic potash	Alc. pot. ext.	0.1%	0.2%	0.6%	1.7%
		Oxidation prod.	0.0%	0.0%	0.1%	0.4%
B)	2 g. rubber+20 cc. benzene+40 cc. O.5*N* alcoholic potash	Alc. pot. ext.	0.5%	0.8%	1.1%	3.5%
		Oxidation prod.	tr.	tr.	0.5%	2.4%
C)	5 g. rubber+50 cc. benzene+50 cc. O.5*N* alcoholic potash	Alc. pot. ext.	0.8%	1.0%	2.3%	7.2%
		Oxidation prod.	0.2%	0.4%	1.5%	6.2%

3. If, in place of alcoholic potash, the rubber is swollen in benzene and then heated with alcohol, the oxidation products are dissolved and may be determined by the usual methods.

It is also evident that the saponification with alkali is not essential, but only the swelling in benzene followed by heating with alcohol. At the beginning of oxidation, oxidation products are formed from vulcanized rubber, which are insoluble in acetone but soluble in benzene. The dissolved oxidation products are extracted by the subsequent heating with alcohol. They dissolve better in a 50:50 benzene-alcohol mixture than in a 20:40 mixture. They are also soluble in ether. On further oxidation, oxidation products are formed which are soluble in benzene-alcohol but insoluble in ether.
4. Extraction with chloroform directly after extraction with acetone, as prescribed in the German methods of analysis, has but little effect on the result of the determination of the oxidation products.
5. The temperature of drying the alcoholic-potash extract or the oxidation products has little influence on the results as is shown by Table III.

Table III

INFLUENCE OF DRYING TEMPERATURE.

Compound: rubber 92.5 parts
sulfur 7.5 parts
Combined sulfur 5.4%

Drying temperature		Quantity found	
Alcoholic potash extract	Oxidation products	Alcoholic potash extract	Oxidation products
105° C.	105° C.	1.2%	0.7%
105° C.	20° C.	1.2%	0.7%
20° C.	105° C.	1.2%	0.7%
20° C.	20° C.	1.2%	0.7%

Systematic Investigation of the Increase in Oxidation Products on Aging and During Vulcanization

It was of great interest to follow the increase in oxidation products systematically: (a) on aging vulcanized rubber, and therefore during the oxidation of the rubber, and (b) during vulcanization.

(a) on aging vulcanized rubber.

A mixture of 92.5 parts F. L. sheets and 7.5 parts sulfur was given a series of cures. After vulcanization the combined sulfur, acetone extract, alcoholic potash extract, and oxidation products were determined. The vulcanized rubber was ground as fine as possible and exposed in glass vessels to diffuse sunlight. After 8, 15, and 24 months the analyses were repeated. The results are given in Table IV. Figure 1 shows some of the results graphically.

These results show that:

1. The percentage of oxidation products increases on aging, and the faster the higher the percentage of combined sulfur.
2. At the beginning of oxidation the alcoholic potash extract and the oxidation products which it contains show a marked increase, while the acetone extract as yet shows no increase. The determination of the oxidation products is therefore a more sensitive method of demonstrating incipient oxidation than the acetone extract alone.
3. If the sample is further oxidized, a portion of the alcoholic potash extract becomes insoluble in ether, the figures obtained have

Table IV

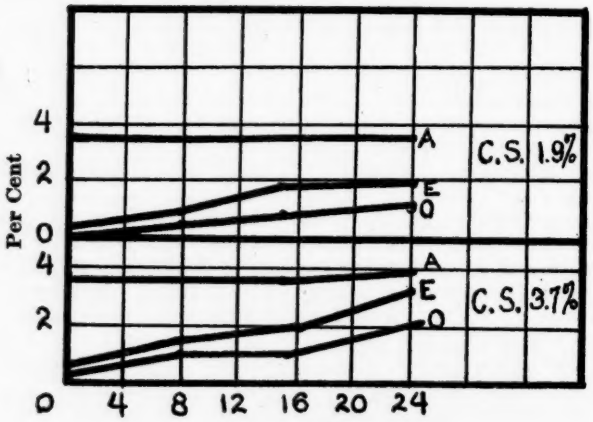
INCREASE OF ALCOHOLIC POTASH EXTRACT AND OXIDATION PRODUCTS ON AGING.

Compound: F. L. Sheet 92.5 parts
Sulfur 7.5 parts

	Organic Acetone Extract	Alcoholic potash Extract	Oxidation Products in alcoholic potash extract
Combined sulfur 1.9%			
Immediately after vulcanization	3.7%	0.6%	0.1%
After 8 months	3.3%	1.0%	0.5%
" 15 "	3.4%	1.9%	0.8%
" 24 "	3.6%	2.0%	1.3%
Combined sulfur 3.7%			
Immediately after vulcanization	3.6%	0.8%	0.2%
After 8 months	3.3%	1.6%	1.1%
" 15 "	3.5%	1.9%	1.1%
" 24 "	4.0%	3.3%	2.2%
Combined sulfur 5.5%			
Immediately after vulcanization	3.4%	0.9%	0.3%
After 8 months	4.0%	3.1%	2.2%
" 15 "	7.9%	(4.0%)*	?
" 24 "	22.5%	(12.4%)*	?
Combined sulfur 6.7%			
Immediately after vulcanization	3.6%	1.2%	0.5%
After 8 months	9.1%	(5.7%)*	?
" 15 "	26.2%	(10.8%)*	?
" 24 "	45.4%	(2.0%)*	?

*A portion of the alcoholic potash extract is insoluble in ether.

Fig. 1
Increase in the alcoholic potash extract and oxidation products on aging.

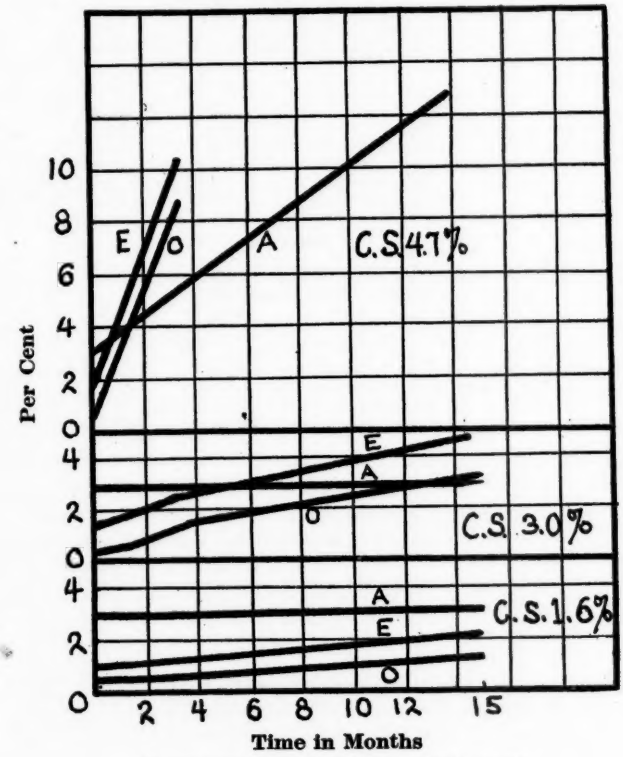


Compound: F. L. Sheets 92.5 parts
Sulfur 7.5 parts
Combined sulfur 1.9 and 3.7%
A=Acetone Extract
E=Alcoholic Potash Extract
O=Oxidation Products

no value, and the oxidation products can no longer be determined accurately by the usual methods.

Further experiments were carried out with numerous mixtures

Fig. 2
Increase in the alcoholic potash extract and oxidation products on aging.



Compound: F. L. Sheets 92.5 parts
Sulfur 7.5 parts
Zinc Oxide 10 parts
Combined sulfur 1.6%, 3.0% and 4.7%
A=Acetone Extract
E=Alcoholic Potash Extract
O=Oxidation Products

of different composition. Table V gives the values obtained for a compound consisting of F. L. sheets 92.5 parts, sulfur 7.5 parts, and zinc oxide 10 parts. A series of cures was run, and the compound finely ground before aging. Figure 2 is a graphic representation of the results. The observations made in the case of the rubber-sulfur compound hold true here also. (See Table IV.)

(b) Attention was now directed to the changes in the alcoholic potash extract and oxidation products during vulcanization. A compound consisting of 92.5 parts F. L. sheets and 7.5 parts sulfur was given a series of cures at 147° C. and then analyzed. The same rubber was previously extracted with cold acetone, compounded as

Table V

INCREASE OF ALCOHOLIC POTASH EXTRACT AND OXIDATION PRODUCTS ON AGING.

Compound: F. L. Sheet 92.5 parts
Sulfur 7.5 parts
Zinc oxide 10 parts

	Organic acetone extract	Alcoholic potash extract		Oxidation products in alc. potash extract
		Ether soluble	Ether insoluble	
Combined sulfur 1.6%				
At first	3.0%	1.1%	.....	0.5%
After 1 1/3 months	3.2%	1.1%	.....	0.4%
" 3 1/3 "	2.9%	1.1%	.....	0.5%
" 15 "	3.3%	2.2%	.....	2.7%
" 24 "	3.6%	3.9%	.....	2.7%
Combined sulfur 3.0%				
At first	3.0%	1.5%	.....	0.7%
After 1 1/3 months	3.0%	1.9%	.....	0.8%
" 3 1/3 "	2.7%	1.4%	.....	0.5%
" 15 "	3.0%	4.9%	.....	3.4%
" 24 "	7.8%	9.6%	trace	8.1%
Combined sulfur 4.7%				
At first	2.9%	1.8%	.....	0.9%
After 1 1/3 months	4.2%	5.1%	.....	3.9%
" 3 1/3 "	5.2%	10.4%	.....	8.8%
" 15 "	14.4%	(11.4%)	28.0%	(7.5%)
" 24 "	26.4%	(13.0%)	50.0%	(10.8%)

before, given a series of cures, and then analyzed. It is well known that extracted rubber oxidizes much faster after vulcanization, and it was interesting to see if this would be indicated in an increase in the amount of oxidation products even during vulcanization. The results are given in Table VI and figure 3.

Table VI

RELATIONSHIP BETWEEN THE ALCOHOLIC POTASH EXTRACT, THE OXIDATION PRODUCTS AND THE DEGREE OF VULCANIZATION.

Compound: F. L. sheets 92.5 parts
sulfur 7.5 parts

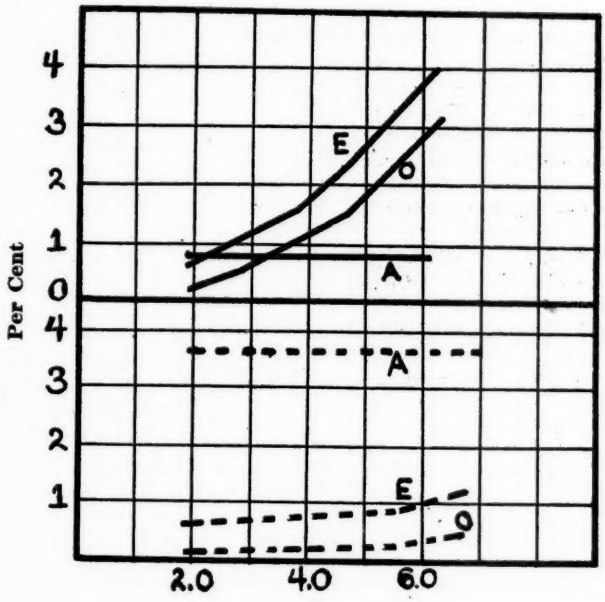
Combined sulfur	Organic acetone extract	Alcoholic potash extract	Oxidation products
1.9%	3.7%	0.6%	0.1%
3.7%	3.6%	0.8%	0.2%
5.5%	3.4%	0.9%	0.3%
6.7%	3.6%	1.2%	0.5%
Compound: F. L. sheets extracted with cold acetone 92.5 parts; sulfur 7.5 parts			
1.9%	0.8%	0.6%	0.2%
2.8%	0.5%	0.9%	0.5%
3.8%	0.6%	1.6%	1.1%
4.7%	0.7%	2.3%	1.5%
6.1%	0.8%	3.8%	2.9%

It is evident that the content of oxidation products increases with the degree of vulcanization, slowly in the case of unextracted rubber and rapidly in the case of extracted rubber, whereas the organic acetone extract remains constant. To this we may add the important fact that:

The proportion of oxidation products in the alcoholic potash ex-

tract increases considerably at the beginning of oxidation, whereas the acetone extract remains constant.[8]

Fig. 3
Increase in the alcoholic potash extract and oxidation products with increasing degree of vulcanization.



Combined Sulfur

-----Compound: F. L. Sheets 92.5 parts
Sulfur 7.5 parts

———Compound: Rubber as above extracted with
Acetone 92.5 parts
Sulfur 7.5 parts

A=Acetone Extract
E=Alcoholic Potash Extract
O=Oxidation Products

In the preceding portion of this work the products which were obtained as a film when the alcoholic potash extract was heated with more alcoholic potash were tacitly designated as oxidation products. Of course it was desirable to prove by analysis that these were really oxidation products, and to learn whether their composition gradually changed with increasing time of cure and during aging.

In the following work vulcanized rubber was used in all cases

prepared from F. L. sheets previously extracted with acetone. In these vulcanizates the percentage of oxidation products increased during vulcanization as well as on aging much faster than in the case of unextracted rubber, large quantities of oxidation products being required for analysis.

A compound consisting of 92.5 parts F. L. sheets previously extracted with acetone and 7.5 parts sulfur was press cured for 2, 3, 4, and 6 hours at 147° C. The combined sulfur, alcoholic potash extract, and oxidation products were then determined. A rather large quantity of oxidation products was obtained by working with 100 g. of rubber. Care was taken to extract these oxidation products with water until an alkaline reaction was no longer obtained; they were then dried in a current of carbon dioxide.

These oxidation products have the appearance of thin, brownish, opaque, rubber-like films, which however, show little extensibility or elasticity. It is notable that these products are insoluble in the ordinary rubber solvents, such as benzene, xylene, benzine (b.p. 40° to 60° C.), and ether, and only swell slightly in them.

The following determinations were made:

1. Ash,
2. Nitrogen (Kjehldahl),
3. Sulfur, by the usual method of Kratz, Flower, and Coolidge,
4. Carbon and hydrogen, by Heslinga's method[9].

At first an attempt was made to determine the oxygen content directly by Ter Meulen's method. This method is very good in the case of organic substances containing no sulfur, but as the oxidation products contain sulfur, difficulties were encountered which could not easily be avoided. Therefore the direct determination of oxygen was finally disregarded, and the oxygen determined by difference. It may be mentioned that the determination of carbon and hydrogen by Heslinga's method may be done rapidly, requiring about an hour for completion.

Table VII

ANALYSIS OF THE VULCANIZED RUBBER AND THE OXIDATION PRODUCTS

Compound: Extracted F. L. sheets	92.5 parts			
Sulfur	7.5 parts			
Analysis of the rubber after extraction with acetone.				
Time of cure	2 hrs.	3 hrs.	4 hrs.	6 hrs.
Ash	0.5%	0.4%	0.4%	0.5%
Nitrogen	0.4%	0.4%	0.4%	0.4%
Combined sulfur	3.7%	5.3%	6.2%	7.3%
Carbon	82.9%	81.7%	80.8%	79.9%
Hydrogen	11.7%	11.7%	11.6%	11.3%
	99.2%	99.5%	99.4%	99.4%
Hydrogen/carbon	8.5	8.6	8.6	8.5
Alcoholic potash extract	0.9%	1.6%	1.6%	2.5%
Oxidation products	0.4%	0.7%	1.0%	1.4%
Analysis of oxidation products.				
Ash	1.8%	1.4%	3.6%	1.6%
Nitrogen	0.1%	0.1%	0.1%	0.1%
Combined sulfur	3.2%	4.1%	5.5%	6.6%
Carbon	80.0%	78.2%	76.0%	77.1%
Hydrogen	11.2%	11.0%	10.8%	11.0%
	96.3%	94.8%	96.0%	96.4%
Oxygen	3.7%	5.2%	4.0%	3.6%

These results permit the following conclusions to be drawn re-

garding the products isolated from the alcoholic potash extract:

1. The ash content is doubtless due to the treatment with alcoholic potash.
2. The products contain combined sulfur.
3. The products contain 3.7 to 5.2% oxygen, and therefore may truly be designated as oxidation products. No importance need be attached to the varying amount of oxygen, since it was determined by difference.

The question is asked, what is the source of this quantity of oxygen during vulcanization. After a six hour cure 1.4% of these oxidation products are formed, containing about 4% of oxygen, so that calculated on the vulcanized rubber we have $0.04 \times 1.4 = 0.056\%$, that is 56 mg. oxygen per 100 g. rubber. Venable and Fuwa[10] have shown that 100 cc. of rubber at atmospheric pressure dissolves 7.3 cc. of oxygen, and Fry and Porritt[11] have recently shown that raw rubber in all probability takes up small amounts of oxygen during milling.

A compound was now mixed, consisting of 92.5 parts F. L. sheets previously extracted with cold acetone, and 7.5 parts sulfur, cured in sheets 1 mm. thick for four hours at 147° C., aged in diffuse light, and the content of oxidation products determined after 1, 2, 4, and 8 weeks. It was shown that even after two weeks a portion of the alcoholic potash extract is no longer soluble in ether. This portion likewise was isolated, extracted with water, and dried in carbon dioxide. Again analyses were made of the oxidation products, both the ether-soluble and insoluble. In the extracted rubber the ash, combined sulfur, oxygen (by difference), nitrogen, carbon, and hydrogen were determined. The results of these analyses are given in Table VIII.

These results permit the following conclusions to be drawn:

1. Ether-soluble and insoluble oxidation products both show a percentage of combined sulfur, which is somewhat lower than that of the extracted rubber. Apparently the decrease in the quantity of combined sulfur is due to the treatment with alcoholic potash.
2. The oxygen content of the ether-soluble oxidation products varies from 3.5 to 5.3%. At best these figures indicate a very slow increase of the oxygen content of the products with increasing oxidation of the rubber during aging. However, the quantity of the oxidation products increases until products insoluble in ether appear.
3. The oxidation products insoluble in ether have a higher content of oxygen than the ether-soluble. Consequently an increase in the oxygen content is noticeable here also.
4. If the ratio of hydrogen to carbon in the extracted rubber is expressed at H:5C, one finds a gradual decrease of this value, which is of great theoretical importance. Although we shall not go into this matter in detail, the following remark may be made.

If the oxygen is attached to a double bond on oxidation, then the ratio H:5C should remain constant. The gradual decrease of the ratio H:5C indicates that the hydrogen is partly removed during oxidation, and probably escapes as water. This theory is in complete accord with the findings of Kirchhof[12], who showed con-

Table VIII

ANALYSES OF OXIDATION PRODUCTS DURING PROGRESSIVE OXIDATION AND STORAGE IN DIFFUSE LIGHT

Compound: F. L. sheets (extracted) ..... 92.5 parts
Sulfur ..... 7.5 "
Vulcanized in sheets 1 mm. thick four hours at 147° C.

	At first	After 1 wk.	After 2 wks.	After 1 mo.	After 2 mos.
Organic acetone extract	0.8%	2.2%	3.2%	4.2%	5.0%
Combined sulfur	6.6%	6.6%	6.5%	6.7%	6.9%
Alcoholic potash extract	1.6%	6.6%	6.1%	6.9%	6.5%
Oxidation products, ether soluble	1.0%	5.8%	4.9%	5.9%	5.0%
Oxidation products, ether insoluble	0.0%	0.0%	4.6%	8.1%	9.5%
Analysis of the rubber after extraction with acetone.					
	At first	After 1 wk.	After 2 wks.	After 4 mos.	After 8 mos.
Ash	0.5%	0.5%	0.5%	0.8%	0.7%
C. S.	6.6%	6.6%	6.5%	6.7%	6.9%
N.	0.4%	0.4%	0.4%	0.4%	0.4%
C.	80.5%	79.9%	79.9%	79.3%	79.1%
H.	11.5%	10.9%	11.0%	10.5%	10.2%
	99.5%	98.3%	98.3%	97.7%	97.3%
O (calc.)	0.5%	1.7%	1.7%	2.3%	2.7%
H:5C		8.2	8.3	7.9	7.7
Analysis of oxidation products soluble in ether.					
Ash	2.0%	2.6%	1.7%	3.0%	2.1%
C. S.	5.5%	5.2%	5.6%	5.3%	5.2%
C.	78.3%	77.3%	78.2%	77.4%	77.2%
H.	10.8%	10.4%	10.7%	10.3%	10.2%
	96.6%	95.5%	96.2%	96.0%	94.7%
O (calc.)	3.4%	4.5%	3.8%	4.0%	5.3%
H:5C	8.3	8.1	8.2	8.0%	7.9
Analysis of oxidation products insoluble in ether.					
Ash	—	—	1.3%	1.6%	0.9%
C. S.	—	—	5.9%	6.1%	6.0%
C.	—	—	76.1%	75.5%	75.1%
H.	—	—	10.6%	9.8%	9.3%
	—	—	93.9%	93.0%	91.3%
O (calc.)	—	—	6.1%	7.0%	8.7%
H:5C	—	—	8.4	7.8	7.4

clusively fifteen years ago that a considerable quantity of water escapes during the oxidation of vulcanized rubber. It may be remarked that this water formation is easily explained by Wieland's oxidation theory[13], according to which the essential feature of oxidation is an activation of hydrogen. It is our opinion then that hydrogen is activated to form water, while, apparently at the same time, a condensation process[14] occurs giving rise to oxidation products, possibly with oxygen atoms as bridges.

An accelerated aging test (Geer-Evans) was made with vulcanized rubber to learn if these oxidation products are formed as on natural aging. A compound consisting of 92.5 parts F. L. sheets and 7.5 parts sulfur was cured in sheets 1 mm. thick for three hours (combined sulfur 5.2%), and aged in a Geer oven at 70° C. for increasing periods of time. The samples were analyzed in the manner previously described. The results are given in Table IX.

In the accelerated aging tests the ether-soluble oxidation products formed have an oxygen content, 3.9 to 5.4%, similar to that of the products formed on natural aging. The sulfur content again is somewhat lower than that of the extracted rubber, but increases with increasing cure. The H:5C ratio falls off slowly. Therefore in the

Table IX

COMPOUND: F. L. SHEET EXTRACTED: 92.5 PARTS; SULFUR, 7.5 PARTS; COMBINED SULFUR, 5.2%. TIME OF HEATING AT 70°C.

	0 hrs.	72 hrs.	168 hrs.	336 hrs.
Increase in weight	——	1.2%	2.7%	4.0%
Organic acetone extract	0.5%	3.3%	5.0%	4.5%
Combined sulfur	5.2%	6.0%	6.5%	6.6%
Alcoholic potash extract	1.2%	6.5%	7.0%	9.8%
Oxidation products, ether soluble	0.6%	5.6%	4.9%	7.6%
Oxidation products, ether insoluble	0.0%	0.0%	6.0%	trace?
Analysis of the extracted rubber.				
Ash	0.5%	0.5%	0.5%	0.5%
N.	0.4%	0.4%	0.4%	0.4%
S.	5.4%	6.2%	6.8%	6.9%
C.	81.8%	79.6%	78.8%	77.1%
H.	11.1%	10.7%	10.3%	9.7%
	99.2%	97.4%	96.8%	94.6%
H:5C	8.1	8.1	7.9	7.4
Analysis of oxidation products soluble in ether.				
Ash	2.0%	2.6%	2.9%	0.9%
C. S.	4.4%	5.0%	5.1%	5.3%
C.	79.1%	78.1%	77.5%	78.5%
H.	10.6%	10.4%	10.1%	9.9%
	96.1%	96.1%	95.6%	94.6%
O.	3.9%	3.9%	4.4%	5.4%

accelerated aging test we have exactly the same process as in natural aging.

The same compound was hung up in the window in the sunlight, and after 10 and 18 days the oxidation products were determined, isolated and analyzed. The results confirmed the previous findings. The oxygen content of the ether-soluble oxidation products varied from 4.1 to 4.6%, and after 18 days there were formed 4.5% of oxidation products insoluble in ether, which contained 6.0% of oxygen.

It was evident that the oxidation products themselves are oxidizable. Those obtained from vulcanized rubber that had been given an accelerated aging test of 168 hours at 70° C. (See Table IX) were kept four weeks in diffuse daylight at room temperature. The oxygen content was then found to have risen markedly, in the case of the ether-soluble products (C. S. 5.1%) from 4.4% to 11.3% and in the case of the ether-insoluble products (C. S. 6%) from 8.5% to 13.3%.

It may be remarked that these oxidation products behave like vulcanized rubber which has the same percentage of combined sulfur and which also is very susceptible to oxidation. Whether oxidation products with a lower sulfur content also oxidize quickly has not been investigated. The difficulty is that such products are obtained in quantities too small for satisfactory elementary analysis.

Application to the Testing of Rubber Goods

The important discovery that during the first stages of oxidation the oxidation products in the alcoholic potash extract increase sooner and more rapidly than the acetone extract may be developed into a very important method of testing rubber goods. In the State Rubber Research Institute at Delft the determination of the oxidation products in the alcoholic potash extract has been often employed during the last few years in establishing the quality of rubber goods. We intend to publish the data collected in more detail, but for the

present we may mention a few important points and give examples thereof.

1. In general it may be said that when the percentage of oxidation products is high the quality of the article is low. Thus for example in the specifications for rubber insulation it was prescribed that the oxidation products in the alcoholic potash extract should not exceed 0.8%. This requirement will be considered conclusive in the new Dutch specifications to be published shortly.

2. In general a connection will be found between the quantity of oxidation products and the physical properties. When the percentage of oxidation products is rather high, the physical properties are usually unsatisfactory. A few examples are given in Table X.

3. If an increase in oxidation products occurs on aging in the Geer oven at 70°C. it can be maintained that the rubber article will soon succumb to increasing oxidation on natural aging. Here, too, the increase in oxidation products is accompanied by a deterioration of physical properties.

The same is true of the steam test which is applied to steam hose. Table X contains some of the results.

Table X

RELATIONSHIP BETWEEN THE PERCENTAGE OF OXIDATION PRODUCTS AND THE PHYSICAL PROPERTIES OF SOME MECHANICAL RUBBER GOODS

	Air brake hose cover		Compressed air hose cover		Steam hose cover	
	Before aging	After 7 days at 70° C.	Before aging	After 7 days at 70° C.	Before steam test 40 hrs. at 4 atm.	After
Organic acetone ext. 7.9%	8.3%		2.9%	2.9%	4.4%	6.9%
Alc. potash ext. 5.2%	5.7%		0.9%	1.3%	1.0%	3.8%
Oxidation products 3.9%	4.4%		0.4%	0.7%	0.2%	2.3%
Tensile in kg/qcm 48	40		99	78	148	37
Elongation at break in % 150	120		355	260	488	220

The air brake hose even before aging showed a high percentage of oxidation products, and the physical properties before aging were correspondingly unsatisfactory.

The compressed air hose showed a low percentage of oxidation products, which increased but little on aging in the Geer oven. Likewise the physical properties remained satisfactory.

The steam hose before steaming had a low percentage of oxidation products and likewise excellent physical properties. In the steam test the hose was subjected to a steam pressure of 4 atm. for a period of forty hours. After this test, which corresponds to service conditions, the percentage of oxidation products had greatly increased, and the physical properties had greatly deteriorated. Therefore this hose promised unsatisfactory service.

Especially in the case of rubber articles whose physical properties it is difficult or impossible to determine, the percentage of oxidation products and the increase on artificial aging is an appropriate means of determining the quality of the rubber. Likewise in the Bierer-Davis bomb test, which is rapidly being adopted, the increase in oxidation products will probably be a much more sen-

sitive measure of artificial aging than the increase in the acetone extract, which has always been determined. Experiments in this direction are under consideration and will be carried out shortly.

Résumé

A method has been worked out for isolating the oxidation products in the alcoholic potash extract of vulcanized rubber. It is shown that, during the initial stages of oxidation, the percentage of oxidation products increases much more rapidly than the acetone extract, and that therefore this fact is to be considered a very important chemical aid in studying oxidation in its initial stages. On further oxidation, oxidation products are formed which are insoluble in ether.

Systematic experiments were carried out on the formation of these products during vulcanization and during the oxidation occurring on aging.

The oxidation products formed during vulcanization and during natural and accelerated aging were carefully analyzed. The carbon and hydrogen were determined by the precise method of Heslinga, while the oxygen was determined by difference. It was found that the oxygen content of the ether-soluble oxidation products was between 4% and 5%, while that of the products insoluble in ether was between 7% and 8%.

Some theoretical considerations were mentioned, and finally the importance of determining the oxidation products in establishing the quality of rubber goods was pointed out, and several examples given.

Notes

[1]*Kautschuk* **3**, 239, 256 (1927).
[2]*Kolloid-Z* **13**, 49 (1913).
[3]*J. Soc. Chem. Ind.* **38**, 339T (1919).
[4]*Giorn. chim. ind. applicata*, **5**, 122 (1923); Rubber Age (New York) **13**, 433 (1923).
[5]Kirchhof, *Kolloid-Z* **13**, 49 (1913).
[6]*Ind. Eng. Chem.* **18**, 1152 (1926).
[7]*Loc. cit.*
[8]It may be remarked in passing that in the presence of certain heavy metal compounds even the unextracted rubber-sulfur compound shows an increase in the oxidation products during vulcanization.
[9]Ter Meulen and Heslinga, *Neue Methoden der organischchemischen Analyse*, **1927**, 7 (Leipzig, Akad. Verlags-Ges.).
[10]*Ind. Eng. Chem.* **14**, 139 (1922).
[11]*Trans. Inst. Rubber Industry*, **3**, 203 (1927).
[12]*Kolloid-Z.* **13**, 49 (1913).
[13]*Handbuch der Biochemie des Menschen und der Tiere*, 2nd Ed. **1925**, II, 252.
[14]It may be remarked that this condensation does not occur due to the influence of sulfuric acid, as similar oxidation products are found in raw rubber on oxidation.

[Reprinted from THE RUBBER AGE (N. Y.),
Vol. 25, No. 4, page 201, May 25, 1929]

An Attempt at a Rational Classification of the Principal Accelerators of Vulcanization*

G. Martin and R. Thiollet

AT the present time there are many accelerators on the market for the vulcanization of rubber, but it is often difficult to choose among them those best suited for a required purpose.

Accelerators are ofte nclassed as slow, medium, rapid and ultra-rapid. These brief terms are entirely unsatisfactory for characterizing clearly the properties of these products, and it frequently happens that two accelerators which have been placed together in one class behave in reality in very different ways and are not entirely replaceable one by the other.

The object of this study is to establish a rational classification of the principal accelerators of vulcanization, which is based not only on their activity but also on their other important characteristics.

The following points will be considered in their order:

(1) The time required for the *fixation* of mixtures at different temperatures.

(2) The time required to bring about vulcanization giving the maxima mechanical properties at different temperatures.

(3) Aging.

(4) These three points of view will be completed by a study of the plasticizing power and of the influence of different charges on the action of the accelerators.

*Translated from Le Caoutchouc & la Gutta-Percha, Vol. 26, No. 302, pages 14494-7, April 15, 1929.

A Study of the Time Required for the Fixation of Mixtures at Different Temperature

The experiments were made on the following type mixture:

Pale Crepe	100
ZnO	5
Palm Oil	1
Stearic Acid	0.5
Accelerator	...
Sulfur	...

The proportions of sulfur and of accelerator used correspond to those commonly used in industrial practice. All the mixtures were prepared from a single master batch, the accelerator and sulfur being incorporated last, in approximately equal lengths of time and at temperatures at which vulcanization does not take place.

Accelerator	Parts of accelerator per 100 parts of rubber	Parts of sulfur per 100 parts of rubber
Zinc isopropylxanthate	2.0	2.0
Tetramethyldisulfide	0.4	1.8
Zinc methylphenyldithiocarbamate	0.7	1.8
Mercaptobenzothiazole	0.7	2.5
Diphenylguanidine	0.7	3.0
Di-*o*-tolylguanidine	0.6	3.0
Phenyltolylxylylguanidine	0.6	3.0
Ethylidene-aniline	1.0	3.5
p-Nitrosodimethylaniline	1.0	3.5
Thiocarbanilide	2.0	4.0
Anhydroformaldehyde-*p*-toluidine	1.0	3.5
Triphenylguanidine	1.0	3.5
Anhydroformaldehyde-aniline	2.0	4.0

Determination of the Points of Fixation

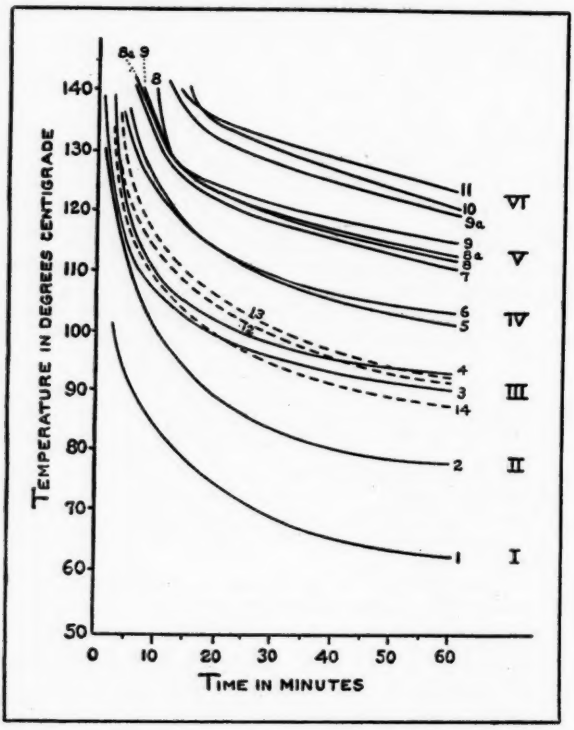
The mixture to be studied was placed in small aluminum molds and press-cured. The molds were taken out every ten minutes and the mixture examined immediately.

It was confirmed that the mixture (2 mm. thick) reached the temperature of the platens in about one minute, the temperature of the platens being controlled by means of a thermometer.

Cures of 10, 20, 30, 40, 50 and 60 minutes were first made at a known temperature. In general when a cure gave a definitely fixed mixture, a cure of 10 minutes less gave a product which had not been fixed. Cures were then made 2, 4, 6 and 8 minutes longer than the lower of these two cures, which permitted the time of fixation to be located within two minutes. For very rapid fixations these cures were repeated at 1 minute intervals.

By this method the time of fixation was determined with an error of

$\pm$ 30 sec. to $\pm$ 1 min. for very rapid fixations.
$\pm$ 2 min. for fixations requiring a cure of 20-30 min.
$\pm$ 5 min. for slow fixations requiring a cure of about one hour.



Representative Curves of Variations of the Times of Fixation as a Function of the Temperatures

1. Zinc isopropylxanthate.
2. Zinc methylphenyldithiocarbamate.
3. Thiocarbanilide.
4. Ethylidene-aniline.
5. Mercaptobenzothiazole.
6. Tetramethylthiuramdisulfide.
7. Phenyltolylxylylguanidine.
8. Diphenylguanidine.

8a. *p*-Nitrosodimethylaniline.

9. Di-*o*-tolylguanidine.

9a. Anhydroformaldehyde-*p*-toluidine.

10. Anhydroformaldehyde-aniline.
11. Triphenylguanidine.
13. Zinc methylphenyldithiocarbamate + anhydroformaldehyde-aniline.
13. Mercaptobenzothiazole + diphenylguanidine.
14. Mercaptobenzothiazole + ethylidene-aniline.

Characteristics of the Point of Fixation

A mixture was considered *fixed* when it has the following properties:

(1) The mixture, without being vulcanized, can be removed from the mold easily. It does not stick to the surfaces and no longer distorts when removed from the mold.

(2) Cut, it can be again united.

(3) A little before the point of fixation the mixture softens when carried quickly to a higher temperature. A little beyond the point of fixation the mixture acquires more nerve when brought quickly to a higher temperature.

The point of fixation thus determined corresponds to that where a mixture will be scorched during milling or in the tube machine.

The determination of the time required for fixation permits the choice from among the list of accelerators of those which will give the greatest safety and will behave best under the conditions required.

Representative Curves

By plotting on the two axes of rectangular coördinates the temperatures as ordinate and the corresponding times of fixation as abscissa, there was obtained a series of curves which show each accelerator according to its rate of fixation of mixtures (see graph).

It should be observed that the accelerators form a very complete range, the curves being spread out regularly over the surfaces bounded by the axes.

The accelerators fall into six groups:

I. Zinc isopropylxanthate.
II. Zinc methylphenyldithiocarbamate.
III. Thiocarbanilide, ethylidene-aniline.
IV. Mercaptobenzothiazole, tetramethylthiuramdisulfide.
V. Disubstituted guanidines, *p*-nitrosodimethylaniline.
VI. Triphenylguanidine, anhydroformaldehyde-aniline, anhydroformaldehyde-*p*-toluidine.

The products within the first group give very rapid fixations, even at low temperatures.

Those of the second group give a little slower fixations and can, with certain precautions, be used in milling operations.

Those of the third, fourth and fifth groups cause fixations still less easily and are still safer to use. It should be observed, however, that tetramethylthiuramdisulfide which, based only on its rapidity of fixation, is classed in the fourth group, causes extremely rapid vulcanization as soon as this once begins. It produces what might be termed an "explosive vulcanization." Scorching is therefore more serious with this product than with an accelerator which causes a more progressive vulcanization.

The accelerators of the sixth group cause fixation only at very high temperatures. Their use is advisable whenever the mixture must remain for a long time at a high temperature, for example in a tube machine.

These results show that for each accelerator an index number, ranging from 1 to 6, can be given which will represent its *rapidity of fixation,* or its *"precocity of action."*

This study emphasizes the essential differences which may exist between two accelerators which are often considered to be part of a single group.

It is in this way that triphenylguanidine and thiocarbanilide, although bringing about vulcanization in equal periods of time, differ essentially by their precocity of action. The case of diphenylguanidine and ethylidene-aniline is similar.

The Effect of the Simultaneous Use of Two Accelerators

It was also considered desirable to show how it is possible to use different accelerators in conjunction with one another and thus obtain different effects. The experiments were made on the type mixture and under the conditions described above.

The proportions of accelerators and of sulfur were as follows.

Accelerator	Parts of accelerator per 100 parts of rubber	Parts of sulfur per 100 parts of rubber
Mercaptobenzothiazole	0.3	2.5
Ethylidene-aniline	0.45	
Mercaptobenzothiazole	0.3	2.5
Diphenylguanidine	0.4	
Zinc methylphenyldithiocarbamate..	0.7	1.8
Anhydroformaldehye-aniline	1.0	

These tests show that *it is possible by a combination of accelerators to obtain a new accelerator of vulcanization whose properties are entirely different from those of its components.*

For example, the diagrams show that:

A mixture containing 3% sulfur and 0.7% diphenylguanidine is not fixed at 105°.

A mixture containing 2.5% sulfur and 0.7% mercaptobenzothiazole is fixed in 45 min. at 105°

But a mixture containing 0.3% mercaptobenzothiazole and 0.4% diphenylguanidine with 2.5% sulfur is fixed in only 23 min. at 105°

The mixture of these accelerators is more precocious than each of its components.

In other cases, on the other hand, *it is possible to retard the precocity of action of rapid accelerators by combining with them another accelerator.* For example: a mixture containing 1.8% sulfur and 0.7% zinc methylphenyldithiocarbamate is fixed in about 10 min. at 100° If to the same mixture 1% anhydroformaldehyde-aniline is added, fixation occurs in about 30 min. at 100°.

These two examples, which can be easily multiplied, give an idea of the importance of a systematic study of mixtures of accelerators.

Such a study will allow the finding of the exact degree of acceleration which should be given to each mixture, according to the particular conditions under which it is used.

These first tests lead to the following conclusions:

The choice of the use of an accelerator should be determined not only by the activity, but also by its precocity of action. An examination of the curves accompanying this article will give information on this subject.

It should be understood that this study applies only to the mixture specified at the beginning of this article and that the introduction of other ingredients is likely to change these phenomena. Nevertheless it has been thought that some rubber technologists would be interested in the results obtained with a somewhat theoretical mixture and that they would find it of some interest to apply to their industrial mixtures the method adopted here.

[Reprinted from THE RUBBER AGE (N. Y.),
Vol. 24, No. 11, page 617, March 10, 1929]

Determination of the Iodine Number of Raw Rubber*

Adolf Gorgas

IN the course of an investigation dealing with the nature of the state of unsaturation of raw rubber, it became necessary to have available a precise and convenient method for determining the iodine number of raw rubber.

Though iodine reacts only slowly with unsaturated compounds[1], chlorine and bromine form both addition and substitution products. In the substitution reactions, the hydrogen halide is evolved, and by addition of potassium iodate, *e.g.*, in the method of MacIlhiney[2], it is possible to determine the hydroden halide formed and thus the quantity of halogen substituted.

In all methods, however, where extensive substitution as well as addition take place, the results are variable and uncertain. Accordingly in the chemistry of fats where the iodine number is of the greatest importance, iodine halides have been used for determining the iodine number, for under certain conditions there is very little substitution. Thus Hübl[3], Waller[4] and Wijs[5] solutions contain iodine chloride and Hanus[6] solution contains iodine bromine. The Hanus method has in fact to a great extent replaced all other methods .

For determining the iodine number of rubber, the Wijs method in the form in which it was modified by Kemp[7] is probably used more than any other. In the Kemp method about 0.1 gram of rubber is swollen in 75 cc. of carbon disulfide, and is then allowed to react for 2 hours at 0° C. with 25 cc. of Wijs solution, *i.e.*, 0.5 *N* iodine chloride in acetic acid.

Hanus solution, *i.e.*, iodine bromide in acetic acid, was also tested by Kemp with rubber under the same conditions as with Wijs solution, and therefore at 0° C. As was to be expected from the smaller activity of iodine bromide, Kemp found that even after 18 hours the addition reaction was not complete. Entirely different results are obtained, however, if the reaction is carried out at room tem-

*Translated from Kautschuk, Vol. 4, No. 11, pages 253-4, November 1928.

perature. At room temperature iodine chloride reacts with many substances having high iodine numbers in such a way that the iodine numbers are too high. Iodine bromide on the contrary reacts with rubber so that at the end of 15 minutes the theoretical iodine number is obtained. Assuming a double bond for each C_5H_8 group, the iodine number of rubber is 372.8.

Of course the Hanus method cannot be applied to the determination of the iodine number of rubber without modifying it to some extent. If the Hanus iodine bromide-acetic acid solution is added to the rubber swollen in carbon tetrachloride, coagulation takes place immediately, and the reaction remains incomplete. The resulting iodine numbers vary greatly, as shown in the table below, and with 25 or 50 cc. of Hanus solution and 0.1 gram of rubber for 15 minutes, the values are too low. On the other hand excellent results are obtained if acetic acid is replaced by carbon tetrachloride. After a brief time of contact between the solution of iodine bromide in carbon tetrachloride and the rubber in the same solvent, the solution becomes turbid, but this does not influence the precision of the determination. Addition of 50 cc. of 0.5 normal iodine bromide in carbon tetrachloride to about 0.1 gram of rubber gives a 50-70% excess of reagent (calculated from the quantity absorbed by the rubber). This 50-70% excess is also customary in the original Hanus method. If the reaction is continued longer than 15 minutes, the iodine numbers are too high.

"Kahlbaum" iodine monobromide and pure carbon tetrachloride, as well as technical carbon tetrachloride, purified by treatment with alcohol and alkali by the method of Schmitz and Dumont[8], were used for preparing iodine bromide solution. The raw rubber which

TABLE I

Comparison of the Iodine Numbers of Raw Rubber Determined With Iodine Bromide in Acetic Acid and With Iodine Bromide in Carbon Tetrachloride

No. of cc. of 0.5 *N* reagent solution	No. of grams of raw rubber	Time of reaction in minutes	No. of cc. of 0.1 *N* $Na_2S_2O_3$ used	Iodine Numbers
25 cc. of iodine bromide in acetic acid	0.1323	15	25.0	239.8
	0.1686	15	28.0	210.7
50 cc. of iodine bromide in acetic acid	0.1350	15	27.4	257.6
	0.1245	15	22.2	226.3
50 cc. of iodine bromide in carbon tetrachloride	0.1562	15	45.9	372.9
	0.0943	15	28.5	383.5
	0.1628	15	47.9	373.5
	0.1771	15	52.1	373.3
	0.0968	30	32.7	428.7
	0.1081	30	36.7	430.8

was used was "total" rubber prepared from Revertex by the method of Pummerer and Pahl[9].

The exact procedure is carried out as follows. Ten grams of iodine monobromide are dissolved in 500 cc. of carbon tetrachloride, and this reagent is preserved in glass-stoppered bottles, under which

conditions it is stable. The determinations are carried out in duplicate.

Approximately 0.15 gram of finely divided rubber is swollen in 50 cc. of carbon tetrachloride in an iodine flask of 300-500 cc. capacity. When the rubber is swollen (24 hours was required with "total" rubber), 50 cc. of iodine bromide reagent are added, with agitation. The reaction mixture is let stand 15 minutes in darkness. At the end of this time, 30 cc. of 10% potassium iodide solution and 100 cc. of water are added, and the solution is then titrated with 0.1 normal thiosulfate solution, with vigorous agitation, until it is colorless. Toward the end of the titration, starch solution is added. The end point is sharp and unmistakable. By agitating during the titration, there is almost no tendency toward emulsification. After the titration the carbon tetrachloride solution appears milky.

A blank test of the reaction solution is carried out under the same conditions.

From the weight s, the titer a of the blank test, the value b of the halogen solution titrated back, and the factor f of the thiosulfate solution, the iodine number is calculated according to the relation:

$$\text{iodine number} = \frac{(a-b)\ (0.01269)\ (f)\ (100)}{s}.$$

References

[1]The recently published method of Margosches, Hinnes and Friedmann (*Z. angew. Chem.* **37**, 335 (1924) does not involve the addition of iodine, but of hypoiodous acid. See also Holde and Gorgas, *Ber.* **58**, 1071 (1925) and **59**, 113 (1926).

[2]*J. Am. Chem. Soc.* **21**, 1087 (1899); Meyer, *Lehrbuch der Org. Chem. Methodik*, 4th Ed. **1922**, 1126.

[3]*Dinglers polytech. J.* **253**, 281 (1884). [4]*Chem.-Ztg.* **19**, 1786, 1831 (1895).

[5]*Ber.* **51**, 750 (1898); *Z. anal. Chem.* **37**, 277 (1898); *Z. angew. Chem.* **11**, 291 (1898).

[6]*Z. Nahr. Genussm.* **4**, 913 (1901).

[7]*Ind. Eng. Chem.* **19**, 531 (1927); *Gummi-Ztg.* **41**, 1978 (1927).

[8]*Chem.-Ztg.* **21**, 511 (1897). [9]*Ber.* **60**, 2152 (1927).

[Translated by J. P. Fahy from Kautschuk, Vol. 5, No. 4, pages 81–8, April, 1929.]

Observations on the Chemical Constitution and Physical Properties of Rubber

Lothar Hock and Guido Fromandi

Some time ago[1] we published the finding that the decrease in the iodine number of rubber on cyclisizing it electrically was accompanied by a marked loss of valuable colloid-chemical properties, and, moreover, that isoprene rubber originally characterized by a low iodine number improved in properties under the influence of the silent electric discharge, while the iodine number increased. These facts suggested that commercially less valuable grades of rubber might owe their inferiority to their essentially lower degree of unsaturation. Therefore the investigation was begun by comparing the known iodine numbers of the best grades of plantation rubber with those of the poorer grades. Pure rubber, as, for example, that prepared by Pummerer's method, is known to have an iodine number very near the theoretical (372.8). In the case of raw rubber each per cent of the rubber hydrocarbon present requires 3.728 units of the iodine number, so that naturally a lower value is to be expected as approximately four units must be subtracted for each per cent of impurity. If we suppose smoked sheets to contain 93% of rubber hydrocarbon, we can ascribe to it an iodine number of only about 347, provided that the impurities do not combine with any iodine, which, however, though not important, is not so. A sample of smoked sheet containing 3.2% of acetone-soluble material and 0.4% of mineral matter besides protein, etc., was found to have an iodine number of 348. Washed Congo rubber containing 5.9% of acetone-soluble material and 1.7% of mineral matter had an iodine number of 329. The iodine number of the acetone-soluble portion was 24, so that 5.9% of extract required approximately 1.4 units of the iodine number; hence the rubber hydrocarbon present had an iodine number of 327.6. If the components of the rubber insoluble in benzene were filtered off and the rubber precipitated twice with acetone and once with alcohol and then dried in a vacuum at 50° C. to constant weight, the iodine number rose to 351.4, thus closely approaching the theoretical value, considering the impurities still present. It is questionable whether or not one may attribute the less valuable properties of this wild rubber to its very slightly lower degree of unsaturation. For the present we shall restrict ourselves to the publication of our results in the following table, with the intention of returning to this question after a detailed examination of a greater amount of material.

Not only are the elastic properties of rubber, which are apparently associated with its power of aggregation, dependent on the colloidal structure or at least on the chemical constitution, but likewise the surface forces between the rubber and the admixed fillers are affected by these structural considerations.

In determining the interfacial tension between rubber and fillers,[4] the values obtained characterize not only the particular filler but also the rubber. Synthetic rubber, which is estimated to be 50% unsaturated, not only possesses faulty physical properties itself, but when compounded would be expected to give different interfacial stresses as compared to first-class plantation rubber, for example, so that

[1] Fromandi, *Kolloid-Beihefte*, **27**, 189 (1928); *Kautschuk*, **4**, 185 (1928). Hock, *Z. Elektrochem.* **34**, 664 (1928).

the experiments have to be carried out with various grades of rubber. Furthermore, the fact must not be overlooked that the interfacial tension may be largely dependent on other substances present; the rubber hydrocarbon itself may not be alone of decisive importance.

TABLE I

IODINE NUMBERS OF SEVERAL RAW RUBBERS

Grade of rubber	Acetone extract in %	Before treatment: Ash in %	Before treatment: Iodine number[2]	Before treatment: Viscosity (flow in sec.)[3]	After precipitating the rubber: Ash	After precipitating the rubber: Iodine number	After precipitating the rubber: Degree of unsaturation	After precipitating the rubber: Viscosity (flow in sec.)[3]	Remarks
1. Smoked sheet	3.2	0.4	348	253	...	...	....	..	....
2. Peruvian (washed)	5.4	2.1	318	117	1.1	357.4	95.8%	94	Iodine number of acetone-soluble substances, 17
3. Congo (washed)	5.9	1.7	329	138	0.7	351.4	94.1%	91	Iodine number of acetone-soluble substances, 24

[2] The iodine determination was carried out by the method of Kemp (*India Rubber J.*, May, **1927**), the iodine no. being the consumption of iodine in grams per 100 grams of substance.

[3] The time of flow of a 3% solution at 25° C. was measured in an Ostwald viscometer with capillary diameter of 0.8 mm.

[4] See previous page. Hartner, *Dissertation*, Giessen, **1929**; Hock, *Z. Elektrochem.*, **34**, 662 (1928).

[Translated from Berichte der Deutschen Chemischen Gesellschaft, Vol. 61, No. 7, pages 1583–1591, July 11, 1928.]

The Purification and Fractionation of Rubber

(7th Communication)[1]

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I—The Alkali Purification of Concentrated Latex. Nitrogenous Impurities in Latex Preserved with Ammonia

It has already been shown that in the purification of latex by alkali, fresh and ammonia-preserved latex behave differently toward alkali.[1] The former is changed even in the cold through decomposition of the proteins (as shown independently by de Vries and Beumée-Nieuwland), whereas the latter first shows evidences of changes at 50°, at which point it creams.

Furthermore, experiments with "Revertex," a concentrated latex, have shown that ammonia-preserved latex is changed in a still different way. Pummerer and Pahl consider the "total rubber," obtained by them from ammonia-preserved latex by the action of alkali, to be free proteins and nitrogen. This view is, however, open to correction. Total rubber is probably fairly free of proteins, but contains nitrogen. The nitrogen content, which is still appreciable even after prolonged treatment with alkali at 50°, varies from 0.15 to 0.4%. This nitrogen was at first overlooked, because it was not detected in a few qualitative Lassaigne tests, nor in a quantitative Dumas determination. Moreover analysis indicated nearly 100% of hydrocarbon. Nevertheless new tests have shown that many samples contained 0.4% nitrogen. When the samples were incinerated with a reduced copper spiral, there was a deficit of 0.4% in the carbon-hydrogen determinations. Accordingly a substance containing 0.4% protein-nitrogen would show a deficit of about 1% on account of the oxygen in the protein. The nitrogen remaining after the alkali purification of ammonia-preserved latex is not protein-nitrogen but amino-nitrogen, which probably is formed by the action of ammonia during long storage. A gel-rubber (0.4% nitrogen) refluxed in benzene for a day with dilute NaOH yielded no amino acids to the NaOH. The neutralized aqueous solution did not give the ninhydrin reaction, nor did the rubber itself when it was boiled with the reagent.

This probable influence of preservation with ammonia on the nitrogen content of "total rubber" was also confirmed by purifying concentrated latex with alkali. Ordinary "Revertex," and, better still, a special "Revertex A" (which did not coagulate like the former when dialyzed in the last step of the purification process and which was, therefore, more suitable than the ordinary Revertex), yielded a total rubber containing only 0.04–0.1% nitrogen (Kjeldahl). It could not be said whether this residue represented unattacked protein in the globules or was due to a high molecular amine. In any case the experiments on Revertex agree fully with the results of de Vries and Beumée-Nieuwland,[2] who in the purification of fresh latex in the tropics were able by the use of cold NaOH solution to reduce its nitrogen to 0.02%. Since methylamine was detected in the latex, there was the possibility that here, too, there was amino-nitrogen held by the rubber.

[1] See *Ber.*, **60**, 2148, 2152, 2163, 2167 (1927).

[2] The results of de Vries and Beumée-Nieuwland have been discussed in detail in *Kautschuk*, 1927, 86.

When this "total rubber" is extracted with ether, there remains "gel-rubber," in which the impurities are enriched in nitrogen up to 0.17%. Further precipitation and study of this gel-rubber is in progress.

A preparation with properties like those of the precipitated gel-rubber can be obtained by allowing the gel skeleton from crepe to swell in benzene, and the clear benzene solution drawn off after a few weeks and precipitated. Analysis of such a preparation showed 0.15% nitrogen. This proportion is also frequently present in sol-rubber from crepe. It is not likely, therefore, that the extraordinarily slight solubility of gel-rubber is the result of a nitrogenous impurity. An effort is being made to remove the last traces of impurities so that the hydrocarbon nature of gel-rubber can be placed beyond a doubt.

II—The Fractional Ether Extraction of Various Preparations of Latex and of Raw Rubber

The experiments described in the present paper, which employed a continuous fractionation in a stream of ether instead of the diffusion method of Feuchter, had for their object determinations of (1) the sol-rubber content of various preparations so that at least its tendency could be learned; (2) the effect of different treatments (caustic soda, acetone extraction, heat), and (3) the composition of pure fractions from raw rubbers, as already done with fractions from latex.[3]

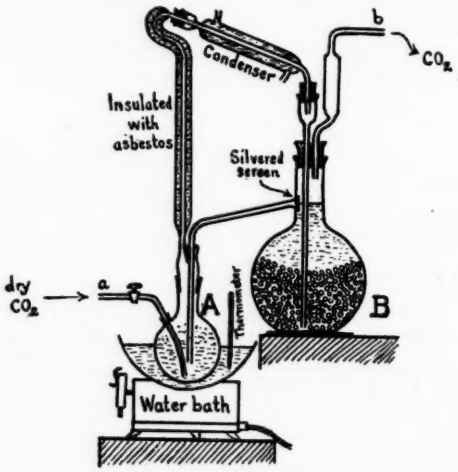

Figure 1—Apparatus for Continuous Extraction

THE APPARATUS—An overflow extractor of the type shown in Figure 1 was used for fractionating the rubber, an apparatus which was first used by Miedel[4] for the same purpose. In the flask *A* (1.5 liters) is dry ether maintained at a lively boil by an electrically heated water bath at 50–60° C. The vapors ascend through a tube insulated with asbestos paper, and are condensed at such a rate that a thin stream of ether flows through the vertical tube to the bottom of the large flask *B* (3.5 liters). Here the rubber is extracted by the ether, the solution flowing in a continuous stream through the overflow tube back into flask *A*. To prevent fragments of gel being carried over, the mouth of the overflow tube is provided with

[3] By preliminary precipitation and purification with alcoholic potash, analytically pure, ether-soluble rubber can be prepared from commercial masticated rubber (see Pummerer and Koch, *Ann.*, **438**, 824 (1924)). Such preparations have very satisfactory nitrogen contents, *i. e.*, less than 0.05%.

[4] Similar to the method of Schacherl for the ether extraction of liquids.

fine meshed silver-plated copper screening. A few centimeters above the level of overflow, there is a small hole in the vertical tube for the escape to *b* of dry CO_2 (air-free) which enters flask *A* at *a*. From here the gas passes through an empty flask and a mercury valve to prevent the sucking back of air through pressure variations or interruptions. The introduction of CO_2 prevents delay in boiling in *A* and oxidation of the rubber. The apparatus is large enough to extract 100 grams of rubber. In about 2 hours all the ether has passed through the system.

A "fraction" is the rubber passing over in 24 hours, except that the first fraction was removed after 6 hours, since in the beginning a relatively large quantity of rubber was dissolved, and the solution in *A* became too viscous. To isolate the rubber, the flask *A* was removed (another being put in its place), most of the ether evaporated at 45° in a CO_2 current and the residue dried in a high vacuum at 45°. The rubber was then preserved in an atmosphere of CO_2.[5]

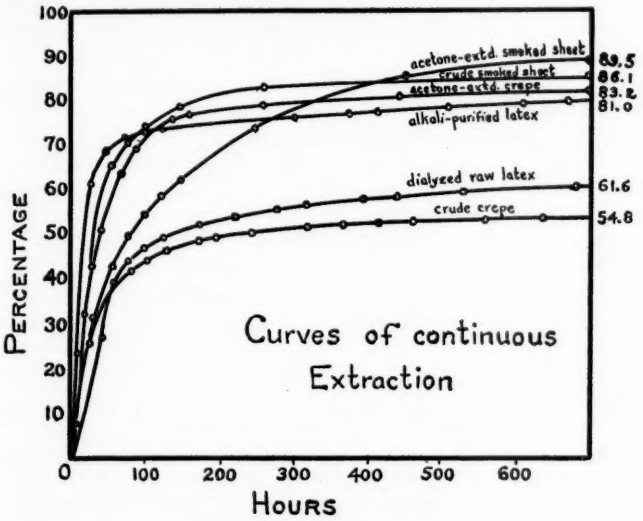

Figure 2

RESULTS—The following kinds of rubber were extracted: (1) purified "total rubber" from preserved latex obtained by the NaOH method of Pummerer and Pahl; (2) dialyzed, ammonia-preserved, raw latex (*Hevea brasiliensis*); (3) crepe; and (4) smoked sheet. The last two were extracted with ether with and without previous extraction with acetone. With acetone-extracted smoked sheet, the ether had to be boiled especially slowly, because of the danger of disintegration. This accounts for the abnormally slow rise of its curve (see Figure 2).

Figure 2 gives the results, the abscissa representing the time of extraction and the ordinate the percentage of the original rubber dissolved by the ether.

(1) "TOTAL RUBBER" ACETONE-EXTRACTED—By letting smoked sheet stand in ether with frequent renewal of the latter according to the Feuchter process, Pummerer and Pahl[6] have separated their "total rubber" into sol- and gel-rubber, 35% gel-rubber being obtained in one case.

In the present work, after continuous extraction for 40 hours (when 65–70% of the total rubber was dissolved) a distinct break in the curve occurred. Beyond this

[5] If in special cases it is undesirable to boil the ether solution of rubber in *A*, the solution can be withdrawn and evaporated. The distilled ether must then be returned to *B*.

[6] *Ber.*, **60**, 2151 (1927).

point relatively little rubber was dissolved, viz., only about 0.2–0.3% each 24 hours thereafter. The residue was gel-rubber. From the tenth to the thirtieth day of extraction, the solubility of the residue remained approximately the same, and the gel-rubber was fairly homogeneous. The solubility is not concerned here, but only the rate of solution. The small quantity of rubber which dissolves subsequent to the time represented by the break in the curve is gel-rubber, because unlike the first four fractions (sol-rubber) it dissolves much more slowly in ether and on standing loses this ability to dissolve in ether.

Fractionation without Coagulation—Latex purified with alkali can, without previous coagulation, be dissolved in solvents and fractionated. This is best carried out by the method of Miedel, hexahydrotoluene being replaced by an another solvent, e. g., acetone, which wets the hydrocarbon particles. For example, 1 cc. of purified latex (10%) is dissolved in 30 cc. of a mixture of hexahydrotoluene and acetone (equal volumes). A considerable part (52–55%) remains undissolved, while the sol-rubber (45–48%) dissolves and can be isolated from hexahydrotoluene solution (first removing acetone by repeated agitation with water). The insoluble portion is in this case not pure gel-rubber, but still contains sol-rubber, since the hexahydrotoluene-acetone-water phase does not dissolve sol-rubber very well.

The experiments show, however, that the insoluble component is present without coagulation, and is probably the shell substance of the latex globule of Freundlich and Hauser. Even unpurified preserved latex, which gives up the rubber hydrocarbon extraordinarily slowly to ordinary organic solvents, e. g., benzene, dissolves in hexahydrotoluene-acetone, but less readily than alkali-purified latex (on account of the protein shell).

(2) Ammonia-Preserved Latex—Freed of water-soluble substances by dialysis, coagulated and extracted with acetone. The curve of this product, which still contained all the protein, rose very slowly, and even after 850 hours showed less extraction than did total rubber after only 50 hours. Here, too, a break in the curve is evident, though less pronounced.

(3) Para Crepe—The course of the curves of extraction of a raw para crepe was extraordinarily similar to the foregoing. The extraction proceeded comparatively slowly, the break in the curve being distinct, as before. It was surprising that after 52% had been extracted, only very small quantities dissolved. The crepe contained, therefore, 48% gel skeleton.

Repeating the experiments with the same crepe previously extracted with acetone showed far different results. Extracted with acetone and dried in a high vacuum, the crepe was very unsuitable for fractionation with ether because it swelled very rapidly and disintegrated into minute flakes which the silvered copper screen did not hold back. After standing 3 months in CO_2, this difficulty was overcome. After this period, the sol-rubber was extracted more quickly and in greater quantity by the ether. After 45 hours 55% passed into solution, and after 150 hours, equilibrium was reached, when but little more dissolved. The residue of gel skeleton after 700 hours was 16.8% of the original material. The residue from the ether extraction of acetone-extracted crepe, which had been stored for 1.5 year after the acetone extraction, was 28.1%, i. e., greater than before. On storage of crepe disaggregated by treatment with warm acetone, a part of the original gel-rubber was formed again.[7]

This method of ether extraction also allowed the preparation in a convenient way of pure sol-rubber from crepe. On acetone extraction, the first fraction of

[7] With regard to the reformation on standing of insoluble rubber from sol-rubber fractions, see Pummerer, *Kautschuk*, **1927**, 234; Bary and Fleurent, *Compt. rend.*, **184**, 947 (1927); Bary, *Rev. gén. caoutchouc*, **4**, No. 31, 3 (1927), which also show the increase of the insoluble part on standing.

crepe was almost nitrogen-free, was colorless, and had a composition corresponding to C 88.18, H 11.94. With unextracted crepe, a product of this purity was obtained only in the third fraction. The high fractions beyond the ninth one were not pure because of slight disintegration in a fibrous condition, e. g., the 10th fraction showed C 87.74, H 11.75, and contained more nitrogen.

The increase in nitrogen content with the fractions is illustrated by the following analyses: *fraction I*, 0.05%; *fraction III*, 0.13%; *fraction V*, 0.20%; *fraction VII*, 0.33%; *fraction IX*, 0.46%; *fraction X*, 0.50%. The residual gel skeleton showed the following analysis: C 81.35, H 11.06, N 2.06, ash 1.02, O residue 4.51. From this the protein content of the gel skeleton of crepe is calculated to be about 13%. To obtain the most nearly pure gel-rubber from crepe, the gel skeleton was swollen in benzene for 6 weeks, the flocks on the clear solution were skimmed off, the solution was evaporated *in vacuo* and dried *in vacuo* at 50° C. The remaining gel-rubber was pale yellowish and tough and showed C 88.23, H 11.88, N 0.15. The C-H determination was in this case carried out without a reduced copper spiral.

When this gel-rubber was kept in a 2% benzene solution for several weeks, it yielded a highly viscous gel, while the second fraction of the sol-rubber, with about the same nitrogen content (about 0.1%), yielded a viscous solution. When freshly prepared, the reprecipitated gel-rubber is completely soluble in ether, though it dissolves more slowly than sol-rubber. On storage, it gradually forms an ether-insoluble base again, which serves to distinguish it from the first sol-rubber fractions. For the sake of completeness, the analysis of the crepe is given: 3.5% water and resin were extracted by acetone, while the dried residue contained C 87.27, H 11.88, N 0.57 (Dumas) and 0.37 (Kjeldahl), ash 0.22. To explain the notable effect of acetone extraction on crepe, which increased the sol-rubber by 30%, a study was made to ascertain whether it was a heat effect or a result of swelling in the acetone.

Five grams of finely divided crude crepe fused in CO_2 were heated at 60° C. for six days. Independently 5 grams of finely divided crepe were digested in acetone at room temperature for 6 days and the rubber separated. Both samples, as well as an untreated sample of crepe, were then digested in ether (1% solution), agitated twice daily, and after 6 days the solution of sol-rubber was poured off from the insoluble part and washed. The first sample gave a highly fibrous residue and a turbid solution. The sample treated with acetone behaved much the same. In the first case 82.3% sol-rubber was obtained, in the second case 56.7%, and from the untreated control sample only 40%. The major part of the effect in the boiling with acetone is, therefore, a heat effect. Actually the swelling effect was too small, because it was measured at room temperature instead of at 56° C., the boiling point of acetone.

The gel skeleton from unextracted crepe (40% yield) was fused and kept in CO_2 for 1 year, and was then digested with ether. More rubber then dissolved in the ether, viz., 4.6%, than the quantity shown by the extraction curve of the previous year. On standing, therefore, ether-soluble sol-rubber was again formed from the gel skeleton. After warming at 60–65° C. for 30 days, this same gel skeleton contained 27.5% sol-rubber.

(4) Smoked Sheet—Though when smoked sheet is digested in ether according to the Feuchter method there is no clear ether solution and nitrogenous sol fractions are obtained, the new continuous extraction method described gives different results. The sol-rubber dissolves very rapidly, the curves showing a pronounced break at 70% extraction after 60–70 hours. The ultimate value after 700 hours was 86% sol-rubber. The high sol-rubber content of smoked sheet is to be ascribed to the fact that in the smoking process the rubber is warmed at 40–50° C. for 6–10 days.

Both initial fractions, which in the case of unextracted crepe were amber colored, were in these latter cases an intense orange. The third fraction was colorless, practically nitrogen-free and analyzed C 88.17, H 11.84 (a pure product). The viscosities, especially those of the lower fractions, were higher than those of the other types of rubber. Here, too, the high fractions contained somewhat more nitrogen. Fractions 1, 3, 5, 7, 9 and 10 showed the following nitrogen values (Dumas): 0.06, 0.14, 0.13, 0.15, 0.25, 0.34. The ether was run off as slowly as possible in order to prevent fibrous material being stirred up into suspension. When the procedure was carried out rapidly the last fractions contained 0.7% nitrogen.

The gel skeleton from smoked sheet (13% yield) analyzed: C 77.89, H 10.90 N 3.26, ash 1.91, 0 residue 6.04. From these the protein content is calculated to be 20.4%. The smoked sheet, after acetone extraction (3.4% water and resin), analyzed: C 87.02, H 11.98, N 0.46 (Kjeldahl), ash 0.3.

III—Relations between Sol-Rubber and Gel-Rubber

The numerical ratio between sol- and gel-rubber must be determined in each individual sample, and depends upon the previous history of the rubber. The transformation of ether-soluble to ether-insoluble rubber and *vice versa*, which has long been familiar to the rubber industry, but which has only now been studied systematically, is readily explained on the assumption that an equilibrium is established,[8] this equilibrium being reached from either direction. In this case it is of little significance whether these two main components are termed sol- (diffusion) rubber and gel-rubber, or α- and β-rubber.[9] However, it has already been pointed out by one of the authors[8] of the present paper that not all the sol fractions take part to an equal extent in the equilibrium mentioned above. For the most readily soluble sol fractions did not, during observations for 1.5 years at room temperature, form any appreciable quantities of gel-rubber, and during 3 months at 0° C. formed only traces. Formation of gel-rubber may be regarded as an orderly colloid-chemical or even crystallographic process which proceeds through the action of extra-molecular forces, and, therefore, which may be considered to be an association rather than a polymerization through primary valences. It is to be hoped that this explanation will lead to more detailed titrimetric studies and studies of the action of azone on various gel-rubbers, the preparation of which has already been described in the present paper (see (4)) and in an earlier paper. The significance of small quantities of impurities in the formation of gel-rubber should also be studied, for the present work shows that the particular sol fractions in which gel formation occurs have the higher nitrogen contents (0.2–0.5%). On the other hand, gel-rubber with only 0.15% nitrogen, i. e., like typical sol-rubber, can be obtained. It is possible that it is merely a lack of nuclei or of catalysts in the first sol fractions which prevents gel formation. If so, it should be possible for all the sol-rubber to take part in the gel equilibrium, as was done by Bary and Hauser, which leads to a simpler conception of the phenomena.

It should be remarked that a method developed by Pummerer, Kroepelin, and Miedel makes possible the quick and easy solution of gel-rubber (and crude rubber containing gel-rubber) in organic solvents, i. e., to peptize the gel-rubber, by adding to the solvents small quantities of bases (NH_3), aliphatic amines (piperidine) or acids (acetic acid, bromobenzoic acid, etc.).[10]

[8] See note 7.

[9] See *Kautschuk*, **1928**, 97. It is not clearly explained whether the gel-rubber of the present paper on the ether-insoluble phase (the gel skeleton of Feuchter) is the β-rubber, which according to the analysis above contains 13–2% protein. It is assumed to be the former, since studies of the equilibrium are to be carried only on the purest fractions.

[10] See *Kautschuk*, **1927**, 1170. The process is patented.

[Translated from Berichte der Deutschen Chemischen Gesellschaft, Vol. 61, No. 7, pages 1591–1596, July 11, 1928.]

The Preparation and Molecular Size of Isorubber Nitrone

(8th Communication)

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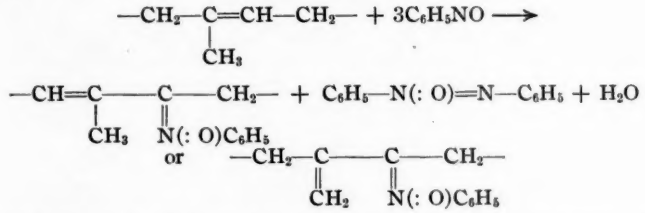
Continuing earlier experiments of Angeli, Alessandri, and Pegna,[1] of Alessandri[2] and of Bruni,[3] the latter and Geiger[4] have recently studied the action of aromatic nitroso compounds on rubber, and have obtained notable results. The earlier experimentors succeeded only in obtaining from nitrosobenzene a compound of the composition $C_{58}H_{61}N_5O_9$. It has recently been proved that one molecule of the nitroso compound for each isoprene nucleus enters the rubber molecule. However, as the earlier investigators have shown, three molecules of nitroso compound react with each C_5H_8 group when the rubber is warmed in benzene on a water bath for 15 minutes. The solution changes from green to dirty green and finally to brown-red. After cooling it is poured into petroleum-ether, whereupon yellow flakes of the composition $[C_{11}H_{11}ON]_x$, decomposing at 135–140°, separate, the yield being 94–98%. This product is evidently formed by the reaction of one molecule of nitrosobenzene with C_5H_8 with loss of 2 atoms of hydrogen. This hydrogen reduces a second molecule of nitrosobenzene to phenylhydroxylamine, which with a third molecule yields azoxybenzene. The latter was isolated from the mother liquor. The rubber derivative which is formed may be regarded as a nitrone of an isorubber:



This compound is characterized by its ability to add one molecule of bromine for each C_5H_8 group, and the further displacement of the nitrosobenzene residue by phenylhydrazine, which serve as proof of its constitution. A greater number of homologs were prepared by Bruni and Geiger.

The present paper also deals with formation of rubber nitrone, the work having been commenced before the appearance of the paper of Bruni and Geiger, the object being to ascertain whether the nitrone is suitable for the separation of sol- and gel-rubber, and whether the molecular size of the nitrone would give a clue to the size of the original rubber molecule. Regarding the former problem, the nitrone does not appear to be an effective means of separating sol- and gel-rubber. The experiments are concerned only with nitrosobenzene, and in general they confirm

[1] *Atti accad. Lincei*, [5] **19**, i, 650 (1910).
[2] *Atti accad. Lincei*, [5] **24**, i, 62 (1915).
[3] *Atti accad. Lincei*, [5] **30**, i (1921); *Kautschuk*, **1927**, 350.
[4] *Atti accad. Lincei*, [5] 823 (1927).

the results obtained by Bruni and Geiger concerning the formation of isorubber nitrone according to the equation above. Of course it is very difficult with nitrosobenzene to avoid a slight absorption of oxygen, especially when a benzene solution of the components is warmed on a water bath for 15 minutes according to the procedure of Bruni and Geiger, which in the present experiments always led to a product containing too much oxygen. It was found that isorubber nitrone, whether dry or in solution, is very sensitive to oxygen, in contrast to rubber itself. The best way to prepare isorubber nitrone is in the cold and with the maximum concentration in benzene and in an atmosphere of CO_2 or nitrogen. Under these conditions the originally highly viscous solution becomes in 20 to 30 minutes a thin liquid, while the reaction is complete in 1–2 days, depending upon the temperature.

Bruni and Geiger emphasized the fact that isorubber nitrone is highly colloidal, but there is considerable doubt whether this is so. Cryoscopic molecular weight determinations were therefore made on isorubber nitrone in benzene and in nitrobenzene. The results were as was to be expected. Even in these familiar solvents, the nitrone gave a depression which indicated a molecular weight of 1200–1400. If a rubber molecule of 8 isoprene units reacts with 8 molecules of nitrosobenzene with elimination of 16 atoms of hydrogen, the calculated value is 1384, which agrees very well with the values above. As in determinations of rubber in menthol, it is necessary to wait 1–2 hours until a constant value is reached, not to make measurements as soon as the solid has disappeared, for in the latter case the values are 1000–2000 higher, probably because of incomplete solution of the micelles. When a condition of molecular dispersion is reached, the values do not change after 14 hours' standing. A study of isorubber nitrone therefore seemed the best way of obtaining an insight into the size of the original rubber molecule. The agreement of the results with the lowest values obtained in menthol, which also indicated 8 isoprene units, is excellent.[5] This value of 8 isoprene units also agrees with x-ray measurements of the elementary cell of stretched rubber.[6]

Experimental

The first experiments on the preparation of isorubber nitrone were carried out under hot conditions, i. e., on a boiling water bath, which conformed to the conditions used by Bruni and Geiger. Since in all cases too little nitrogen was found, the concentration was varied, so that with a 5% solution of rubber, the product contained 7.3% nitrogen (calculated 8.09%). When all air was excluded, somewhat more than 3 molecules of nitrosobenzene were used, and the concentrated solution was kept cold, and the reaction allowed to continue for a long time, the rubber then reacted completely and the nitrogen content was the theoretical value. In many cases the carbon value also conformed with the theoretical, though not always, since slight oxidation took place at times. It is doubtful whether Bruni and Geiger, working with hot solutions, obtained an analytically pure product, though no definite conclusion is warranted since they have so far failed to publish their analytical data. Since the exact reproduction of most reactions of rubber is always very difficult, exact directions are given in the following text for a definite substance, but not all factors which influence the results, such as its previous history and the time of swelling, have yet been eliminated.

Preparation of Isorubber Nitrone

One and one-half grams of rubber were finely divided and dissolved in 60 grams of benzene, which requires considerable time, depending upon the kind of rubber.

[5] Pummerer, Nielsen, and Gündel, *Ber.*, **60**, 2167 (1927). For the molecular weight determinations in camphor see the appendix.

[6] Bary and Hauser, *Kautschuk*, **1928**, 97.

With sol-rubber a homogeneous solution is obtained in 1 day, while gel-rubber usually requires 3–4 days. The solution is treated in the cold with 8.1 grams of nitrosobenzene in 15 cc. of benzene, the resulting mixture being of a concentration corresponding to 2% rubber. The air in the reaction flask is expelled by nitrogen or CO_2, the flask is closed and thoroughly shaken. Addition of the nitrosobenzene solution to the rubber solution changes the blue-green color of the former to a deep green, within 15–20 minutes (or within 20–30 minutes with gel-rubber) the reaction mixture loses its viscosity, after a few hours the mixture becomes turbid and a precipitate settles out. After standing 16–22 hours at room temperature the reaction is ended, the mixture now being red-brown. At this stage the mixture is filtered from the sticky precipitate, the filter being bathed in a stream of nitrogen. The filtrate is then added slowly in a thin stream to a large quantity of dry petroleum-ether (boiling below 40° C.), which precipitates the product. The precipitated nitrone is in the form of beautiful, bright yellow flakes which settle rapidly. The liquid is decanted, the nitrone is washed 3–4 times with petroleum-ether, is then filtered on a non-fibrous filter, an atmosphere of nitrogen again being maintained to prevent oxidation. After repeated washing with petroleum-ether, the nitrone is removed with a metal spatula to a glass dish, which is then placed in a desiccator containing $CaCl_2$ and pieces of paraffin and in an atmosphere of CO_2. The desiccator is slowly exhausted until the petroleum-ether is evaporated. A high vacuum is then maintained for about 6 hours until the last traces of solvent are removed.

For the molecular weight determinations, the products were purified by repeated solution in warm benzene and reprecipitation with petroleum-ether. Analysis of the purified products then showed no evidence of an incomplete reaction. In most cases there had been some oxidation.

In this way isorubber nitrone was prepared from sol-rubber and from gel-rubber obtained from smoked sheet and from crepe. The following analyses were obtained:

	Carbon	Hydrogen	Nitrogen	Sample
$[C_5H_6:(C_6H_5NO)]_x$	72.26	6.41	8.09	calculated
Sol-rubber (smoked sheet)	76.04	6.90	8.05	I
Reprecipitated	75.95	6.92	8.13	Ia
2nd preparation	74.52	6.82	8.17	II
3rd preparation	75.10	7.02	8.17	III
Gel-rubber (smoked sheet)	74.24	6.67	8.16	IV
Sol-rubber (crepe)	74.67	6.67	8.20	V
Gel-rubber (crepe)	75.12	6.74	8.23	VI

In the preparation of gel-rubber from crepe (where the crepe gave only a jelly-like swelling), the reduction of the viscosity by the nitrosobenzene in the first one-half hour was especially striking. In general gel-rubber reacts more rapidly than does sol-rubber.

Description of the Nitrone

When the nitrone is analytically pure, it dissolves fairly easily and completely in cold benzene. In agreement with Bruni and Geiger, there was no evidence of a crystalline structure. It is noteworthy that, on standing, the solubility of the nitrone gradually diminishes, as in the case of rubber itself, which may be regarded as evidence of aggregation. Chloroform and chloroethylene dissolve the nitrone readily, nitrobenzene dissolves it less easily, while it is barely soluble in petroleum-ether, ligroin, or ether. When it is let stand in the air for several days, or when oxygen is passed through its benzene solution, oxygen is gradually absorbed. Thus when dry oxygen was passed for 6 hours through a solution at 55°

C., a product containing 1.25% oxygen was obtained. Not much more oxygen than this was absorbed on long standing.

Molecular Weight Determinations

(See foregoing table)

Product I (sol-rubber from smoked sheet): 0.1467 g. in 13.20 g. C_6H_6 (K = 5.1): $\Delta\tau$ (after 1 hr.) 0.0425°; M = 1330. $\Delta\tau$ (after 13 hrs.) 0.040°; M = 1420.

Product Ia: 0.1455 g. in 18.06 g. $C_6H_5NO_2$ (K = 7.07):[7] $\Delta\tau$ (after 5 hrs.) 0.043°; M = 1320.

Product II: (1) 0.1449 g. in 1806 g. $C_6H_5NO_2$: $\Delta\tau$ (after 4 hrs.) 0.051°; M = 1120; (2) 0.1363 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 5 hrs.) 0.042°; M = 1260.

Product III: 0.1424 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 1 hr.) 0.043°; M = 1300.

Product IV (gel-rubber from smoked sheet): 0.1510 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 2 hrs.) 0.041°; M = 1440.

Product V (sol-rubber from crepe): (1) 0.1443 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 8 hrs.) 0.045°; M = 1260. $\Delta\tau$ (after 18 hrs.) 0.44°; M = 1285. (2) 0.1375 g. in 18.06 g. $C_6H_5NO_2$; $\Delta\tau$ (after 10 hrs.) 0.040°; M = 1350.

Product VI: (1) 0.1398 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 24 hrs.) 0.042°; M = 1310; (after 33 hrs.) 0.042°; M = 1310. (2) Control at another concn.: 0.1092 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 5.5 hrs.) 0.034°; M = 1260. $\Delta\tau$ (after 24 hrs.) 0.0335°; M = 1280. (3) After repeated precipitation: 0.1460 g. in 18.06 g. $C_6H_5NO_2$: $\Delta\tau$ (after 5 hrs.) 0.045°; M = 1270.

Appendix

In the molecular weight determinations in camphor which have recently been published, there is an error to be corrected in the molecular weight column.[8] Ether-sol-rubber (warmed continuously for 8 days at 100°) gave a value of 1580, not 580, in other words, practically the same value as before warming.

Staudinger has recently attempted to explain in another way these molecular weight determinations of rubber and gutta-percha[9] which he has incidentally confirmed. He, too, established the fact that the hydrocarbons remain intact (see page 2168). He assumes that they decompose the camphor "catalytically," though hexacontane and carotene do not do this[10] and though measurements lasted only five minutes. This attempt at an explanation is upset by the proved fact that the concentration of the camphor solution within rather large limits (1 : 4 to 1 : 20) has no influence on the experimentally determined mean molecular weight (see page 2169). This was confirmed in recent experiments on rubber by Andriessen and on gutta-percha by Brunswig. The values obtained with gutta-percha varied from 1130 to 1250.

If the same melting point is determined several times in succession, it hardly changes, which likewise contraverts the idea of catalytic action. Only when these successive determinations are continued frequently does the depression become materially greater, owing to continued sublimation of the camphor. On account of this sublimation, a correction factor must be introduced if the experiments require much time, in which case the constancy of the results is very satisfactory. According to Staudinger, in determinations of cyclorubber in camphor, the sublimed camphor contained an impurity (water or terpene or both), and decomposition of the camphor was assumed from this fact. Because of the importance of this point in the problem of hydrocarbons of high molecular weight, the purest recrystallized camphor (m. p. 177.6° corrected) was used in the present work. With this camphor, the purest sol-rubber and gutta-percha (both oxygen-free) showed the mean molecular weights already observed, without there being any appreciable

[7] Neither of these determinations was carried out in nitrogen, as were the succeeding ones.

[8] Pummerer, Nielsen, and Gündel, *Ber.*, **60**, 2172 (1927).

[9] Miedel, *Kautschuk*, **1927**, 232.

[10] Zechmeister and v. Cholnoky, *Ann.*, **455**, 78 (1927).

quantity of impurities in the sublimed camphor. The few crystals of sublimed camphor in the tube had a m. p. of 177.6° in the gutta-percha experiment. When 5 grams of camphor were heated with 1 gram of rubber for 15 minutes at 183°, a few milligrams of camphor sublimed, the melting point of which was depressed around 0.8°. A weighed $CaCl_2$ tube gave no evidence of water. On further heating completely pure camphor sublimed. The traces of impurities, which are here somewhat high, are not measurable as depressions in the mass of fused mixture, while the depressions were 2.5 to 12°.

[Translated from Kautschuk, Vol. 5, No. 1, pages 2–5, January, 1929.]

The "Freezing" of Raw Rubber

A. van Rossem and J. Lotichius

The "freezing" of rubber is a phenomenon which has been known for a long time in the rubber industry, but there has been no satisfactory investigation from a scientific point of view. By freezing is meant the tendency of raw rubber to become hard and opaque when stored for a long period in the cold, and to become elastic and translucent again when warmed.

In 1918, Bunschoten[1] showed that when frozen rubber thaws, its density diminishes, and later van Rossem[2] made a more extensive investigation of this phenomenon. The opinion was expressed by Pickles[2] that "This is an extremely interesting observation, and in my opinion these results indicate that a very important change in structure or orientation occurs at this point, comparable perhaps with crystallization in ordinary liquids."

Soon afterwards Katz[3] undertook x-ray studies of rubber, and with Bing[4] came to the conclusion that frozen rubber is in a partially crystallized state and that these "crystals" disappear when the rubber thaws. In view of this discovery, it was of great importance to undertake a more exact investigation of the freezing of rubber and, at the suggestion of Katz, to correlate the physical properties and the x-ray data.

The Thawing of Frozen Raw Rubber

As a beginning, the phenomena observed on thawing frozen rubber were studied, a few samples of first latex sheet which had been preserved in a cool room since 1915, and which were frozen hard, being examined.

Small pieces of frozen samples were heated over a period of two hours at constantly increasing temperatures in an air bath, and after cooling to room temperature the density, hardness, and light absorption were measured.

The density was measured by the method of Caspari[5] in water at 15° C. The hardness was measured at room temperature by the Shore durometer. The light absorption was measured with an extinction meter (instrument of Kipp, Delft). The e. m. f. of a thermo-current, generated by a beam of light which fell directly on a thermopile, was measured potentiometrically. The beam of light was then passed through the rubber and the e. m. f. was again measured. The ratio of the two e. m. f. values gave a measure of the light absorption, expressed as a percentage of the impinging light.

As an example from a large number of curves, the density, hardness, and light absorption of first latex sheet as functions of the temperature are shown graphically in Figure 1.

It is evident from these curves that the density, hardness, and light absorption each show a sharp fall at the same temperature, viz., 36–38° C.

Similar measurements were made of first latex sheets which had not been frozen. The relations between the three properties and the temperature were characterized by the straight line course of the curves, without any sharp break as before.

[1] Bunschoten, *Mededeelingen van den Rijksvoorschtingsdienst t.b.v.d. Rubberhandel en de Rubberijverheid*, 3de Serie, s. 37 (1921)

[2] Pickels, *India Rubber J.*, **67**, 69 (1924).

[3] Katz, *Naturwissenschaften*, **13**, 410 (1925).

[4] Katz and Bing, *Z. angew. Chem.*, **38**, 439 (1925).

[5] Caspari, *India Rubber Laboratory Practice*, London, **1914**, 104.

These results are easily explained if it is assumed that frozen rubber is partially crystallized. At 36–38° C. the crystals melt, with a resulting rather sudden increase in the transparency, diminution in the hardness, and increase in volume (as with many organic compounds).

The samples which had not been frozen, and which therefore contained no crystallized component, showed no changes of the above kind in the same temperature range.

If frozen rubber is partially crystallized, its absorption of liquids should be less than that of the same rubber in the thawed state, for it is probable that crystals of rubber behave more or less like fillers and therefore impede the adsorption of liquid.

Accordingly the water absorption of two similar pieces of smooth sheet was measured, one sample being kept frozen and the other being thawed by heating to 40° C. In Table I are the increases in weight in water at 27° C., calculated for 1 gram of rubber. These data show that the water absorption of frozen rubber actually was much smaller than the absorption of the same thawed rubber.

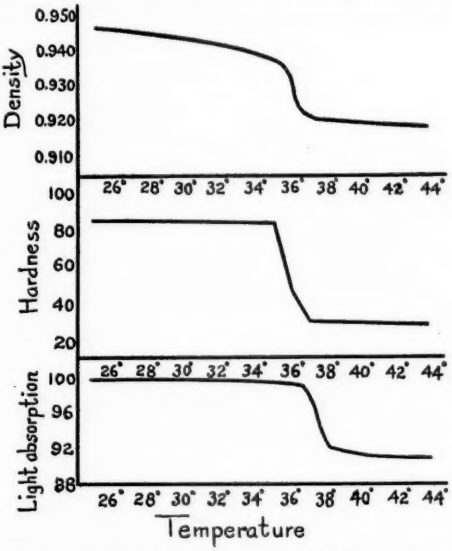


Figure 1—Density, Hardness, and Light Absorption as Functions of the Temperature of First Latex Sheet

TABLE I

WATER ABSORPTION BY FROZEN AND BY THAWED RUBBER

No. of days	Frozen	Thawed
2	8.2	37.6
4	11.5	46.7
10	15.4	55.5
16	15.4	61.4
21	15.4	66.0

If frozen rubber is partially crystallized, it should show on "melting" a certain heat of fusion. If it were possible to determine this heat of fusion, a new proof would be had of the partial crystallization of frozen rubber.

As is known, frozen rubber is very rapidly thawed by swelling in organic liquids like benzene or toluene, the opaque frozen rubber soon becoming transparent. If therefore the heats of swelling of frozen and of thawed rubber in an organic solvent are measured, the difference of the two values should represent the heat of fusion a of the frozen rubber, i. e.,

$$Q_{\text{frozen}} - Q_{\text{thawed}} = q$$

These heats of swelling were measured with a Bunsen ice calorimeter, an apparatus which is well suited to the measurement of small quantities of heat. Toluene was chosen as solvent, 2.5 grams of frozen and of thawed first latex sheet being dissolved in 12 cc. of toluene. The results are summarized in Table II, the values being the averages of two concordant values.

The heats of fusion of these three samples agree very well, with an average of $q = 5.05 \pm 0.28$ g.—cal. per g. of rubber. This is a further proof of the existence of a crystallized component in frozen rubber.

TABLE II

HEATS OF SWELLING IN TOLUENE AT 0° C. OF FROZEN AND OF THAWED RUBBER

Type of rubber	Heats in g.-cal. per g. rubber: Q frozen	Q thawed	Heat of fusion q
First Latex sheet (Ceylon, 1919)	6.53	1.23	5.30
First Latex sheet (Java, 1919)	6.60	1.50	5.10
First Latex sheet (1916)	5.30	0.55	4.75
		Average	5.05

The magnitude of this heat of fusion of crystalline rubber is for the present still undetermined because the proportion of this crystallized part in rubber is unknown.

In 1919 curves showing the change of density with the temperature for a few samples of frozen first latex sheets were determined precisely, and these samples have now been measured again.

Figure 2 shows two curves for one of the samples. The very remarkable fact is evident that the curves do not coincide but show two important differences which are evident from an examination of Table III. The same results were fully confirmed with four other samples.

TABLE III

CHANGES IN THE MELTING POINT AND IN THE DENSITY OF FIRST LATEX SHEET DURING NINE YEARS (1919 TO 1927)

Property	Year	Value
Melting point	1919	31–33° C.
	1927	35–37° C.
Decrease in the density at the melting point	1919	0.029
	1927	0.031
Difference in density at 20° C. frozen at 40° C. thawed	1919	0.014
	1927	0.012

It is probable that the rise in the "melting point" depends upon the growth of crystals. Though the earlier experiments of Pawlow,[6] who believed that he demonstrated differences of 4° C. to 7° C. in the melting point of crystals of 0.5 mm. and 2μ of various organic compounds, such as salol, antipyrine, etc., have been challenged by Meissner,[7] the influence of the size of crystals on the melting point has been proved beyond doubt by Tammann.[8] It is reasonable to attribute the differences in melting points of the rubber samples to the growth of crystals. Assuming this, it is easy to understand why the decrease in density at the melting temperature remains unaltered (see Table III). Such a decrease depends upon the quantity of the crystalline substance and the latter does not change, large crystals merely growing at the expense of small crystals.

The density of the first latex sheets, whether in a frozen or in a thawed condition, increased to the same extent, viz., 0.012 from 1919 to 1927. This fact is difficult to explain. It might be from polymerization, as assumed several investigators, like Bary and Fleurant,[9] and Hock.[10] However, this much used and misused expression does not throw much light on the phenomenon.

[6] Pawlow, *Z. phys. Chem.*, **65**, 34 (1909).
[7] Meissner, *Z. anorg. allgem. Chem.*, **110**, 169 (1920).
[8] Tammann, *Ibid.*, **110**, 166 (1920).
[9] Bary and Fleurant, *Compt. rend.*, **184**, 947 (1927).
[10] Hock, *Z. Elektrochem.*, **34**, 662 (1928).

Artificial Freezing of Raw Rubber

It was obviously of great importance from a technical point of view to study the factors which govern the freezing of rubber. Accordingly several samples of old, frozen first latex sheets were thawed in water at 100° C., and were then artificially frozen by storing (1) at 4° C. and (2) at −10° C., the progressive increases in density and in hardness being measured. The results on one of the samples are shown in Figure 3.

The density and the hardness before thawing are shown by the straight lines in Figure 3. The curves reveal that the increases in the hardness and density ran approximately parallel to one another.

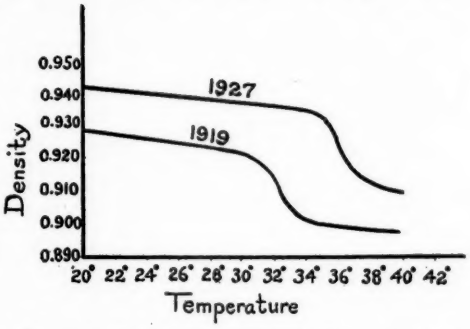


Figure 2—Relations between the Density and the Temperature of Frozen Sheet in the Years 1919 and 1927

After 3 to 4 days at −10° C. the rubber acquired its original hardness and its original density, while at 4° C. this increase was slower and lasted about 9 to 10 days. It became opaque again and had the same appearance as normally frozen rubber. When this rubber, artificially frozen at 4° C. and at −10° C., was maintained for a few moments at room temperature, it immediately became transparent and flexible again, i. e., it "melted."

To study this phenomenon more closely, first latex sheet which after thawing had been kept frozen for 9 days at −10° C. was warmed very slowly in water and the changes in its density and hardness as a function of the temperature were determined. The results given in Figure 4 show a sample of first latex sheet which in a normally frozen condition had a melting point of 35–37° C. The melting point was now at a much lower temperature and covered a wider range.

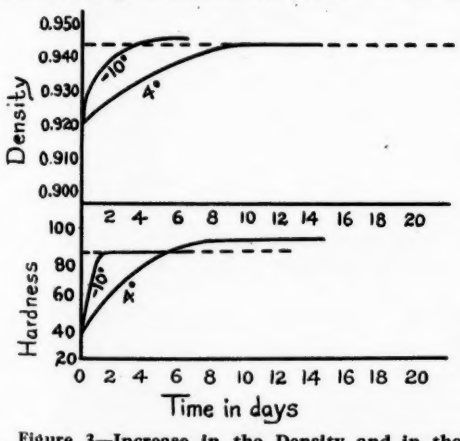


Figure 3—Increase in the Density and in the Hardness of Thawed First Latex Sheets at 4° C. and at −10° C.

It is believed that this remarkable phenomenon depends upon the size of the crystals. Crystallization in general depends upon two factors: (1) the number of nuclei, (2) the growth of these nuclei.

The number of nuclei increases with the degree of cooling, with an optimum at a definite temperature. On freezing at −10° C. and at 4° C. the number of nuclei is great but the crystals are small, much smaller in fact than those in rubber which has been kept for more than 10 years.

This explains the fact that the melting point after thawing and subsequent freezing is so different from the original melting point. On storing, the melting point would then gradually rise. Accordingly, several samples were kept for a

long time at −10° C. During 6 months the melting range increased only slightly.

Since the samples of frozen rubber had been thawed at 100°, it was possible that too high a temperature had been used, and that the growth of crystals had been impaired. Accordingly, several samples of rubber were thawed at different temperatures, viz., 40°, 70°, 100°, 130°, and 160° C. These samples were frozen at −10° C. and at 4° C. There were no significant differences, though the samples which had been thawed at 40° froze somewhat more rapidly. By thawing again, it was proved that the low melting range, as in Figure 4, did not depend upon the temperature of the first thawing.

Moreover after storing for a long time at −10° C. and 4° C., no significant differences were evident. The experiments prove therefore that the temperature of the first fusion has no great influence on the second fusion curve. It is therefore probable that the position of the fusion curve is governed by the size of the crystals.

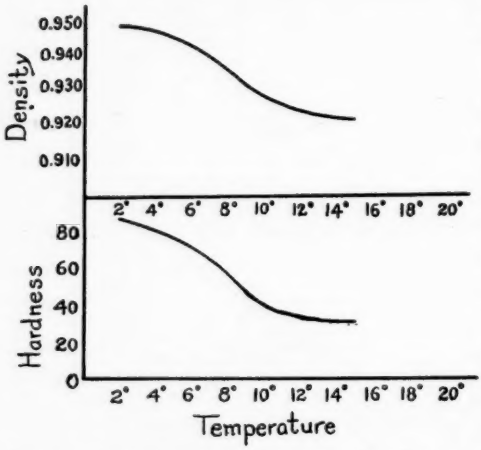


Figure 4—Fusion Range of First Latex Sheet Thawed and Newly Frozen at −10° C.

The growth of crystals in a supercooled liquid increases as the temperature increases, and it seems reasonable that at −10° C. and 4° C. the growth of crystals is slow and that at higher temperatures, e. g., 12° C., the growth is more rapid. Experiments in this field are in progress.

Rubber samples were then plasticized for increasing lengths of time (5 to 60 min.) on a hot mill, and were afterward frozen at −10° C. and at 4° C. Here too the differences in the rates of freezing were insignificant, while again the second fusion curve was at a much lower temperature range than was the initial curve. It was necessary in this case, too, first to determine experimentally the optimum temperature of crystal growth.

Experience shows that samples of plantation rubber under the climatic conditions of Europe differ considerably in their tendency to freeze, and experiments are already under way to ascertain the factors which influence this phenomenon.

It must be made clear, however, that like every crystallization process, the freezing of rubber depends upon two factors, the number of crystalline nuclei and the growth of the latter.

Though factors like the temperature and plasticity have no great influence on the number of crystalline nuclei, it is easily possible that these factors influence the growth of the crystals. A closer study of the factors in their influence on freezing will be possible only when the optimum temperature of growth has been determined experimentally and the growth of the crystals can be followed continuously in its relation to the displacement of the fusion curve.

Conclusions

The experiments lead to certain general conclusions.

1. Measurements of the changes in density, hardness, and light absorption show

that all three properties suddenly decrease at the same temperature, doubtless as a result of the fusion of a crystalline component.

2. Measurements by means of a Bunsen ice calorimeter show that hard frozen samples of rubber have a definite heat of fusion.

3. The "melting point" of frozen rubber changes as time goes on, a phenomenon which may be explained by the growth of crystals.

4. A study of the freezing of raw rubber at $-10°$ C. and at $4°$ C. shows that freezing occurs in a few days, and that such rubber melts at a lower temperature than rubber which has been kept frozen for several years, phenomena which are explainable by the ordinary known laws of crystallization.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 4, No. 5, pages 413-423, February, 1929.]

The Tackiness of Unvulcanized Rubber

T. L. Garner

This work is mainly directed to the action of light on raw rubber and on rubber to which has been added a small quantity of an antioxidant by as little milling as possible.

There has been considerable work done in connection with the tackiness and oxidation of raw rubber, but until recent years the connection between the two has been very little understood, and is not fully comprehended today. The accelerating action of copper and other materials on the rate of deterioration of rubber was very early recognized, but it was not until 1906, when Herbst (*Ber.*, **39,** 523 (1906)), by passing dry air through an approximately one per cent solution of purified Para rubber in benzene, maintained at the boiling point under a reflux, was able to prepare and separate two products both having the formula $C_{10}H_{16}O$. This work formed the first real advance of our knowledge of the mechanism of oxidation and appeared to show that atmospheric oxidation of raw rubber involves no breaking down of the octadiene ring.

Discussions as to the interrelation of tackiness and oxidation did not begin until 1909 when Spence (*Kolloid-Z.*, **4,** 70 (1909)) working with Funtumia rubber, found that coagulation with sulfuric acid gave a tacky rubber. As a result of his experiments, he concluded that the resin content, oxygen content, and capacity for adding on bromine were not noticeably different for tacky and sound samples of raw rubber, and that therefore tackiness and oxidation were not necessarily related. The next year Aeuri (*Le Caoutchouc*, **7,** 4371 (1910)) discovered that ultra-violet light caused tackiness and also oxidation, and in the same year Henri showed that it was the ultra-violet part of the spectrum which was particularly harmful to rubber. He found that dissolved rubber reprecipitated was more susceptible to ultra-violet light than untreated rubber, and also that no apparent action took place *in vacuo*. Fickendey (*Kolloid-Z.*, **11,** 81 (1911)) showed that tackiness developed in sunlight was arrested if oxygen was withdrawn; the addition of the more readily oxidizable tannin to the extent of 2.5% during coagulation greatly retarded the inset of tackiness on exposure.

Berstein (*Kolloid-Z.*, **12,** 193 (1913)) concluded that the primary action of ultra-violet light on rubber was disaggregation, followed by oxidation due to the formation of ozone from atmospheric oxygen by the action of the light. Working on solutions, he found that disaggregation, shown by reduced viscosity of the rubber in solution, was brought about by the influence of ultra-violet light in the absence of oxygen. This theory was widely supported; and about the same time, as a result of his experiments, van Rossem arrived at the following conclusions: (1) Oxidation of rubber by heat in solution as well as in the solid state is always a secondary state preceded by a depolymerization. (2) The depolymerization by heat is catalytically accelerated by oxygen, and this acceleration must be considered as the primary process causing tackiness of rubber.

In recent years a research was conducted on the action of ultra-violet light on rubber by Asano (*India Rubber J.*, **70,** 307 (1925)), in which he gave a detailed list of the literature of the subject. According to his experience, raw rubber became par-

tially insoluble in all rubber solvents when it was exposed to light. He carried out exposures in inert gases and in air and found that in both cases part of the rubber was rendered insoluble in benzene. The film exposed in an inert gas turned white and opaque. Separating the soluble portion in each case and preparing a solution of known strength, he found that the solution viscosity was practically the same in each case, and considerably lower than that of the original rubber. He stated that light below 2250 A. U. had a special action on rubber, giving a white, opaque, polymerized rubber, while above 2250 A. U., an oxidized, transparent rubber was formed. Using light, the shortest wave-length of which was 2351 A. U. and focusing on a small portion of a rubber solution in benzene, he was able to precipitate an insoluble film of rubber, but light of shortest wave-length 2434 A. U. had not this effect.

Porritt and Fry (*Trans. Inst. Rubber Industry*, **3**, 203 (1927)) have recently shown the effect of heat and milling on the solution viscosity of rubber and clearly showed the effect of a small quantity of oxygen upon this property.

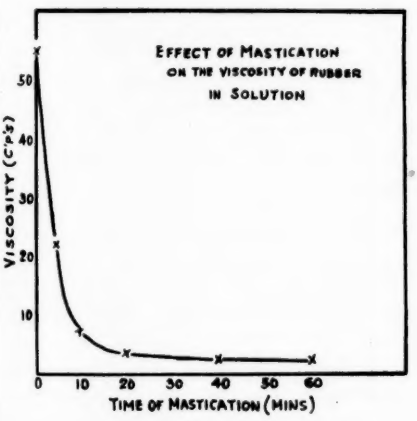


Figure 1

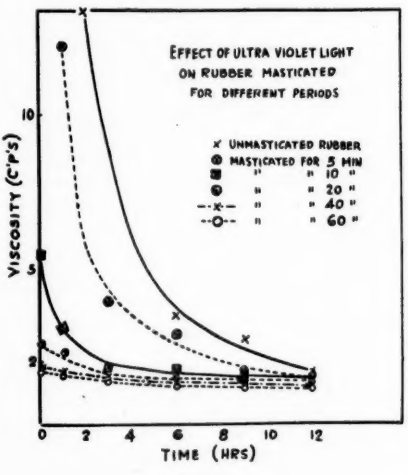


Figure 2

The experimental part of this research aims at substantiating and amplifying some of the previous work on the properties usually associated with tackiness and then the effect of antioxidants.

For the determination of viscosities, a viscometer of the Ostwald type was used, carefully standardized by means of sucrose solutions as recommended by Bingham and Jackson (U. S. Bureau of Standards, *Scientific Paper*, **298** (1917)), and all viscosities are given in centipoises. The viscosity of water at 20° C. is approximately one centipoise. One per cent solutions were used throughout, these being prepared by dissolving one gram of rubber in 99 cc. of toluene. The temperature of the viscometer bath was maintained at 40° C. ± 0.1° C. The quartz lamp used was of a type made by the British Hanovia Quartz Lamp Co. It was possible with this lamp to shut off all visible radiation by means of a special glass screen, but in these experiments the full radiation from the lamp was used.

A sample of pale crepe rubber was masticated for an hour, samples being removed at intervals. No cutting was done on the mill during mastication and the weights removed did not appreciably affect the main bulk of the rubber. The temperature of the rolls was approximately 135° F. The effect of this mastication on the vis-

cosity of one per cent solutions is shown in Figure 1 and Figure 2 shows the effect of ultra-violet light on the samples of rubber masticated for varying periods. In these curves for the sake of clarity the upper points have been omitted. It has often been stated that more accurate viscosity measurements are obtained by using a well-masticated sample of rubber, and this must be so, for in the case of such a rubber the solution viscosity has been reduced already to such a figure that light can have little further effect upon it.

With the lamp a temperature of about 40° C. was maintained in the region of the samples exposed, so that it was necessary to determine the part played by the heat treatment. Samples of pale crepe rubber, finely sheeted and dried in the dark over sulfuric acid *in vacuo* were exposed to ultra-violet light, and at the same time similar samples were heated in the dark to 38° C. ± 0.1. The two curves obtained (Figure 3) show how small is the effect of the heat compared with that of light. The more rapid effect of the ultra-violet light on a solution is shown in Figure 4, a five-hour exposure reducing the viscosity of a one per cent solution to

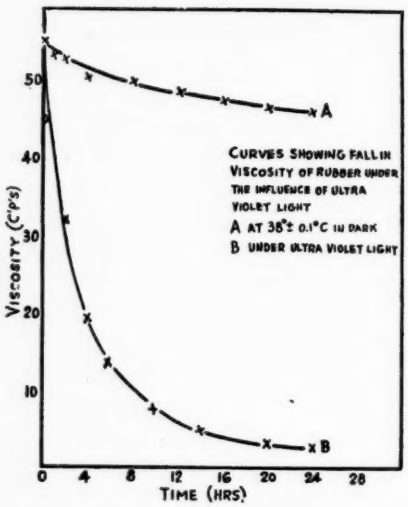


Figure 3

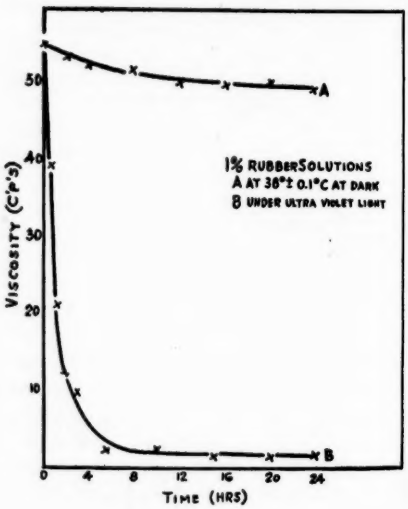


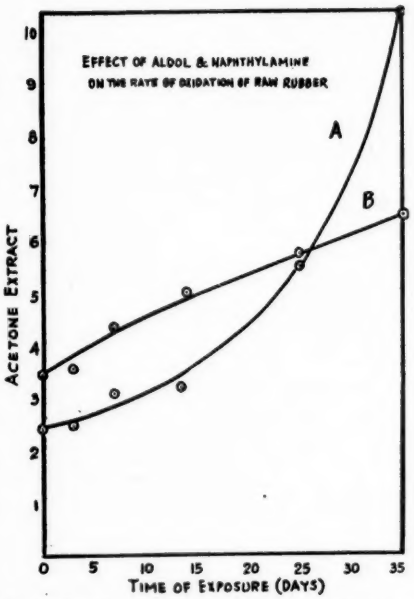
Figure 4

the same extent as a twenty-four hour exposure of the solid rubber. The fall in viscosity of the solution, when heated in the dark, is of the same order as in the solid state. These experiments were carried out in an excess of air, but the samples were enclosed in thin glass tubes sealed to prevent evaporation from the exposed solutions. By treating the solid rubber similarly, an accurate comparison was possible and the absorption of light by the tubes could be neglected. It should be noted that under these conditions no insoluble rubber was formed, all the solid samples dissolving in toluene with occasional shaking after standing in the dark for a day or two.

The effect of excluding oxygen on the production of tackiness was tested in the following manner. One-gram samples of rubber were accurately weighed out into tubes, five samples being prepared. The tubes were connected up in series, and a supply of pure nitrogen passed through them; to assist in the removal of traces of oxygen from the surface of the rubber a current of steam was passed round the tubes by means of jackets. The nitrogen was passed for four hours, and at the end of

that time it was assumed that all oxygen had been removed. The rubber in one tube was then taken out and dissolved in toluene to form the blank solution for viscosity determinations. Two tubes were sealed up in the atmosphere of nitrogen and through the other two air was drawn; these four were then exposed under the lamp. Tubes were removed after twenty and forty hours, and it was found that in the case of the nitrogen-filled tubes there was no apparent tackiness, but in air the rubber was very tacky and gellified, particulary after forty hours' exposure. The strips in nitrogen were slightly whiter than initially, but in air had turned a bright golden yellow. The strips exposed in air were readily soluble in toluene, giving solutions of low viscosity, but those exposed in nitrogen gave much insoluble rubber, especially after forty hours' exposure. The soluble portion had a viscosity approaching that of the pure solvent.

A repetition of the experiment using carbon dioxide gave the same result. With a similar exposure of a one per cent solution, from which air had been removed, the viscosity fell to a value only slightly above that of the pure solvent, no insoluble rubber being precipitated. There is, therefore, a big difference in the effect of light on rubber and its solutions in the absence of oxygen. The experiment in the solid state in an atmosphere of nitrogen was repeated with rubber prepared according to a slight modification of the method of Pummerer and Koch (*Ann.*, **438**, 295 (1924)). The rubber was a selected pale crepe, which was first extracted for five minutes with ether and then for twenty-four hours with acetone. The rubber was then dissolved in toluene and precipitated with alcohol and the above extractions repeated three times. Finally, the rubber was dissolved in toluene and a mixture of alcohol and toluene added until about 30 per cent of the rubber was precipitated. The rubber in the remaining solution was then separated and used for the experiment. On analysis it conformed to the correct empirical formula for the rubber hydrocarbon, and after exposure to ultra-violet light in an atmosphere of nitrogen as previously described, it was again analyzed and found to conform to the correct empirical formula. There is, therefore, only a physical aggregation taking place, the product gradually became more and more insoluble in the usual rubber solvents.



A, milled rubber; B, milled rubber + antioxidant.
Figure 5

The statement that the empirical formula is obtained means within the limits usually accepted. Some deviation from the calculated values for carbon and hydrogen, viz., 88.24 and 11.76, respectively, is always noted. For instance, one analysis gave hydrogen 12.12 per cent and carbon 87.46 per cent, a deficiency of 0.42 per cent. After exposure in nitrogen the figures obtained were 12.08 per cent and 87.38 per cent, respectively, the deficiency being 0.54% which is substantially the same result.

The introduction of a small quantity of oxygen to a tube containing nitrogen gave, on exposure, a degree of visible tackiness comparable to that obtained in air, but in this case a small quantity of insoluble rubber was formed. The production of a tacky surface seems, therefore, to be due to an oxidation process, and that there is in addition the depolymerizing and polymerizing action of the light.

In view of the relation between oxidation and tackiness, it is an obvious step to see how far, if at all, antioxidants are of use in the prevention of the latter.

A sheet of pale crepe rubber was prepared and other samples containing, respectively, $^1/_4$ per cent manganese sulfate, $^1/_2$ per cent aldol-α-naphthylamine. The milling required to introduce these substances was made the same in each case and the uncompounded rubber milled to the same extent. The three samples were exposed to light in sunny weather, and it was proposed to trace oxidation changes by means of the acetone extract and tackiness by the solution viscosity. This was possible in the case of the uncompounded sample and also in the case of the sample containing manganese sulfate, but the aldol-α-naphthylamine rendered the sample containing it partially insoluble in toluene after a few days, and almost completely so after several weeks. It was, therefore, impossible to show whether the aldol-α-naphthylamine retarded the tackiness of rubber by means of the solution-viscosity test, but judged by the acetone extract its retarding action on oxidation changes was observed (Figure 5). α-Naphthylamine had a similar effect. The insoluble rubber formed seemed to be of the oxidized variety. It should be noted that in the case of the rubber containing antioxidant, the acetone extract includes the amount of the latter extracted.

A further attempt to find the effect exerted by antioxidant substances on the solution viscosity was made in the following manner. A one per cent solution of pale crepe rubber in toluene was prepared, and to separate portions of this was added 0.5 per cent of various antioxidants dissolved in toluene in the cold. (Unfortunately, some antioxidants were not sufficiently soluble in cold toluene to be included in this test.) Viscosities were taken, and then the solutions exposed to the action of ultra-violet light in sealed tubes containing an excess of air for two hours and viscosities again taken. The results with seven antioxidants are given in Table I.

TABLE I

Antioxidant	Viscosity: Before exposure	Viscosity: After exposure	% Reduction	Order
1	17.39	10.63	38.8	3
2	23.49	11.82	49.7	6
3	23.81	13.27	44.2	4
4	22.15	12.02	45.7	5
5	20.42	17.46	14.5	1
6	25.70	20.37	20.8	2
7	20.98	7.94	62.1	7

If it is assumed that the solution viscosity is a measure of tackiness, then Table I gives the order in which these antioxidants resist the formation of tacky rubber. This is not, however, the order in which they resist oxidation changes in rubber mixings, for No. 5 antioxidant, the best in this table, is the worst antioxidant when incorporated in a rubber mixing. No insoluble rubber was formed in any case.

The behavior of an antioxidant with regard to oxidation changes, therefore, seems to be no guide to its action in the prevention of tackiness. It was originally intended to use the test given above to form some idea of the value of an antioxidant in a rapid manner, but this was not possible. The rubber containing the antioxidant was greatly affected from the point of color, but this property can be better observed in a white compounded mixing.

Conclusion

In ordinary cases of exposure of rubber to air and light, the processes of tackiness and oxidation run concurrently, but it was possible to reduce the viscosity of a rubber solution in the absence of oxygen by exposure to ultra-violet light. Such a solution gave on evaporation a depolymerized rubber which readily absorbed oxygen. The introduction of a small quantity of oxygen into a tube containing rubber in an atmosphere of nitrogen gave, on exposure, a rubber apparently as tacky as if exposed in air. The only difference was that part of the rubber was rendered insoluble. The action of light was partially polymerization and partially depolymerization, and the extent of each was determined by the conditions obtaining. The presence of oxygen was necessary to secure a tacky film of rubber, and thus confirmed Porritt and Fry's experiment. Little change took place in the solution-viscosity of rubber or its solution when heated to 40° C. in the absence of light. Under the conditions of these experiments no insoluble rubber was obtained by exposing solutions or uncompounded rubber in air, but in inert gases the formation of insoluble rubber of the polymerized, oxygen-free type, noticed by Asano, was observed to increase with the length of the exposure. The insoluble rubber formed when rubber, protected by the incorporation of an antioxidant, was exposed to light did not seem to be of this type, but the transparent, oxidized rubber obtained by Asano in some of his experiments. At the same time the rate of oxidation judged by the increase in acetone extract did not progress to the same extent as with unprotected raw rubber. The protection afforded by antioxidants from the point of tackiness (judged by solution-viscosity) appeared to bear no relation to their value in prevention of oxidation changes.

One important point must be borne in mind in connection with the technical application of antioxidants. It has been shown that the latter will protect a rubber in such a way as to prevent depolymerization and oxidation changes to some extent, thereby assisting the formation of an insoluble and presumably polymerized rubber, which is not observed in ordinary cases of exposure. Thus an insoluble rubber layer is formed on the surface of the exposed rubber and destroys the tackiness. Consequently, the use of much antioxidant in a mixing which is required to retain its tackiness while exposed in a factory to light for some time, does not appear to be good practice. Samples of mixed rubber containing 1 per cent of antioxidant were found to lose their surface tackiness much more rapidly than the blank mixings on exposure to light; the surfaces of the former became hard and dry.

The following theory is suggested. On mastication of raw rubber globules are partially burst and also depolymerization of the hydrocarbon occurs, resulting in reduced solution-viscosity. The tackiness of masticated rubber is due to the action of oxygen upon the depolymerized hydrocarbon and cannot appear until the latter is available. Thus on exposure of unmasticated rubber, the surface layer must first be depolymerized and then oxidized. Antioxidants in protecting the rubber from depolymerization and consequent oxidation allow the polymerizing action of light to become the superior effect. Consequently, in a tacky rubber, repolymerization of the oxidized and depolymerized layer occurs to some extent and in proportion as polymerization occurs, so tackiness is lost. In ordinary masticated rubber, the oxidized depolymerized rubber is distributed through the whole, but in special cases only the surface may be affected.

Tackiness will be destroyed by substances which exude to the surface and cover the tacky layer with a greasy film, e. g., stearic acid, or by substances which assist in any way the polymerizing action of light. Hence, where tackiness is desired, circumstances leading to these results should be avoided.

[Reprinted from The Journal of Physical Chemistry, Vol. 33, No. 2, pages 226–243, February, 1929.]

The Absorption of Oxygen by Rubber

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BELL TELEPHONE LABORATORIES

It is generally believed that the most important factor in the aging of rubber is the absorption of oxygen from the atmosphere. It is also generally agreed that no entirely satisfactory accelerated aging test for rubber goods is available. Because of the increasing importance of rubber in modern industry it is essential that a knowledge of the mechanism of the absorption of oxygen by rubber be available, not only for the development of tests which will accurately foretell the natural life of rubber goods, but also for the development of rubber compounds of superior aging qualities. It is surprising how little such information is available and how many conflicting views concerning the influence of oxygen absorption on the aging of rubber exist.

In view of the very complete survey of the literature dealing with aging prior to 1921 made by Geer[1] in his paper concerning the well-known aging test developed by Geer and Evans,[2] it seems unnecessary to include a complete review in this paper. Since the work to be reported in this paper was completed, Tener, Smith, and Holt[3] have reported on a study of the aging of rubber made at the Bureau of Standards and have included a review of the literature. The earliest paper referred to in these bibliographies is that by Spiller,[4] but reference should also be made to a still earlier paper by Hoffman[5] who studied the changes taking place in gutta-percha during its natural life. He concluded that gutta-percha absorbs oxygen from the air and simultaneously changes into a hard brittle material.

The work reported in this paper deals with the absorption of oxygen by rubber and the physical changes associated therewith, and is therefore rather closely related to that of Peachy[6] and of Peachy and Leon.[7] Since the work here reported was completed, Leon and Lister[8] have published an account of a continuation of the earlier work of Peachy and Leon. These investigators had no means for keeping the pressure constant throughout the reaction and their rate curves as a result contain irregularities which cannot be interpreted. Also, in most cases the samples used by them were deposited as films from solution and may not have been in the same physical state as the original material. The method used in the work here reported provides for constant conditions of oxygen pressure and of temperature throughout the determination and is described in detail later.

Eaton and Day[9] attempted to study the absorption of oxygen at room temperature by following the change in weight of samples exposed to oxygen, but concluded that the change in weight did not represent the amount of oxygen absorbed because of losses of volatile oxidation products from the samples. Their curves are of

[1] *India Rubber World*, **1921**, 887.
[2] *Rubber Age*, **11**, 345 (1922).
[3] *Technologic Paper*, Bureau of Standards, No. **342**.
[4] *J. Chem. Soc.*, **18**, 44 (1865).
[5] *Ibid.*, **13**, 87 (1861).
[6] *Ibid.*, 1103 (1912).
[7] *Ibid.*, **37**, 55T (1917).
[8] *Ibid.*, **46**, 220T (1927).
[9] *Ibid.*, **38**, 3339T (1919).

interest, however, in that they show that the oxidation of rubber at room temperature is autocatalytic. Jones,[10] Henriques,[11] and Ditmar[12] find also that the gain in weight of samples is not proportional to the amount of oxygen absorbed as volatile oxidation products are given off. Ditmar finds that in some cases samples actually lose weight during oxidation.

Bruni[13] studied the absorption of oxygen by sealing samples in glass tubes containing oxygen, but in this case rates have very little significance as the progressively diminishing pressure of oxygen in the tubes was not followed during the reaction. Marzetti[14] studied the absorption of oxygen by sealing samples up in tubes contain-

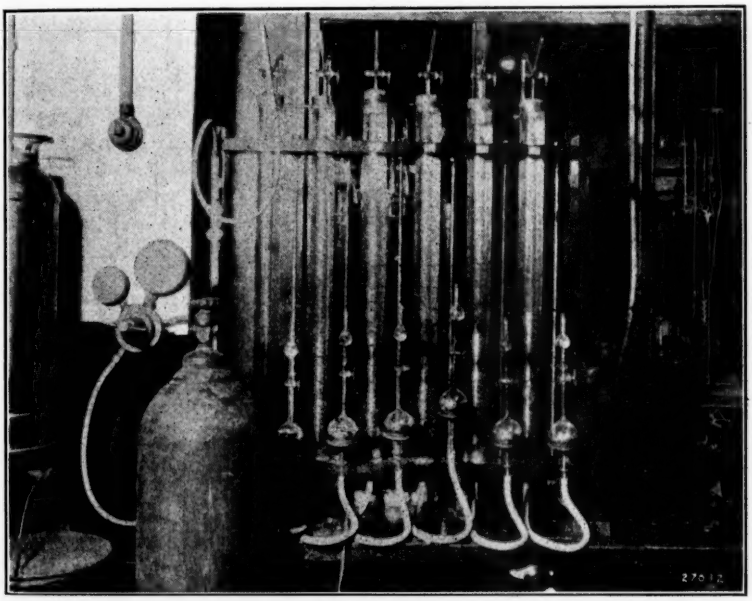


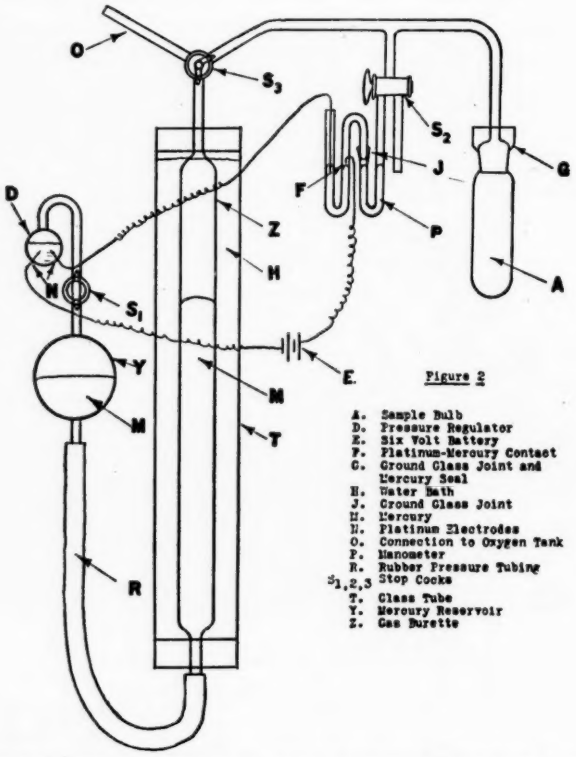
Figure 1—Photograph of Absorption Apparatus

ing known amounts of oxygen and measuring the residual amount of gas left in the tubes after keeping them at high temperature for some time. He finds that the various tendencies for different rubbers to age depend upon the rates with which oxygen is absorbed. Others who consider natural aging as the result of absorption of atmospheric oxygen are Miller,[15] Burghardt,[16] Ahrens,[17] and Jones.[10] On the other hand, Parks[18] considers aging a more complex phenomenon. Asano[19] finds that raw rubber exposed to light in the absence of oxygen undergoes a change. Jecusco,[20] however, does not entirely agree with Asano upon the effect of light.

[10] *Ind. Eng. Chem.*, **17**, 871 (1925).
[11] *Chem.-Ztg.*, **19**, 235 (1895).
[12] *Gummi-Ztg.*, **20**, 628 (1906).
[13] *India Rubber J.*, **63**, 814 (1922).
[14] *Giorn. chim. ind. applicata*, **5**, 122 (1923).
[15] *J. Chem. Soc.*, **18**, 273 (1865).
[16] *J. Soc. Chem. Ind.*, **2**, 119 (1883).
[17] *Kunststoffe*, **3**, 478 (1914).
[18] *Rubber Age*, **7**, 64 (1926).
[19] *India Rubber J.*, **70**, 307 (1925).
[20] *Ind. Eng. Chem.*, **18**, 420 (1926).

Bertrand[21] believes that tackiness may be due to a kind of fermentation caused by an organism. Tener, Smith, and Holt[3] believe that internal changes which deteriorate rubber take place in the absence of oxygen. Their results will be discussed later.

The general conclusion of those who have studied the aging of rubber is that the absorption of oxygen, if not the sole cause of natural aging, is the most important factor. The two most widely used accelerated aging tests, the Geer[2] test and the bomb test developed by Bierer and Davis,[22] have been developed on this basis.



Detailed Sketch of One System of the Apparatus Shown in Figure 1

However, as pointed out by Glancy,[23] Vogt,[24] Park,[25] and later by Tener, Smith, and Holt,[3] these tests are not entirely satisfactory. The extent of aging in these tests is determined by measuring the deterioration of tensile strength, and it is probable that changes in tensile strength under the conditions of these tests are not always proportional to extent of chemical degradation. Additional curing at the temperatures of the tests is known to result in an increase in tensile strength during the tests even though the samples have absorbed oxygen and aged. Also tensile strength measurements cannot be made highly accurate and are subject to gross

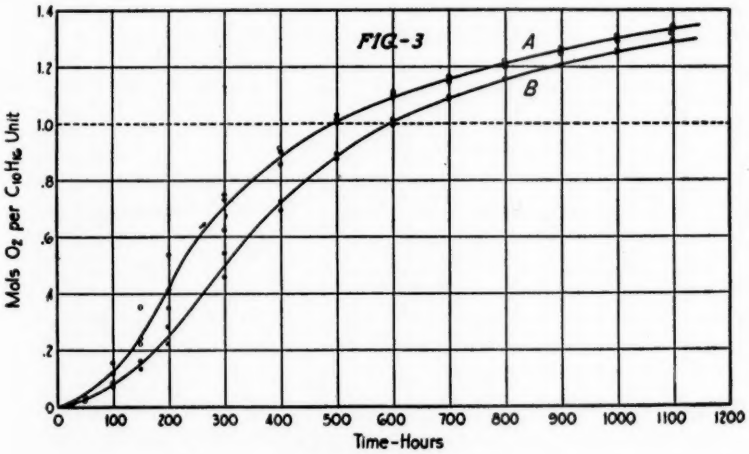
[21] *India Rubber J.*, **35**, 620 (1908).
[22] *Ind. Eng. Chem.*, **16**, 711 (1924).
[23] *Ibid.*, **17**, 869 (1925).
[24] *Ibid.*, **17**, 870 (1925).
[25] *Rubber Age*, **7**, 64 (1926).

error in some cases. Suitable samples are not always available, and since the test destroys the sample, repetition of the test at intervals involves the assumption that all of the samples of a series originally have the same tensile strength.

The work here reported was planned to show the relation between natural aging of rubber and rate of oxygen absorption with the object of developing an accelerated aging test based directly on rates of oxygen absorption. To show this relationship the effect on oxygen absorption of several of those factors which are known to influence the natural aging of rubber has been studied. The results obtained have encouraged us to make a more complete investigation of the mechanism of oxygen absorption. The factors discussed in this paper include the following:

1. Surface area;
2. Cure;
3. Effect of milling;
4. Effect of anti-agers;
5. Effect of ozonized oxygen;
6. Effect of absorbed oxygen on tensile strength;
7. Effect of heating in inert gases on tensile strength.

The apparatus used involves special means for keeping the oxygen pressure surrounding the sample constant, as preliminary experiments showed that in a system of constant volume small enough to permit sufficiently accurate measurement of absorbed oxygen the pressure cannot be considered constant during the experiment. The apparatus used is shown in Figure 1. It consists of six individual systems,



Reproducibility of Results

A. Compound 90% smoked sheet,6- hour cure
B. Compound 90% smoked sheet,4- hour cure

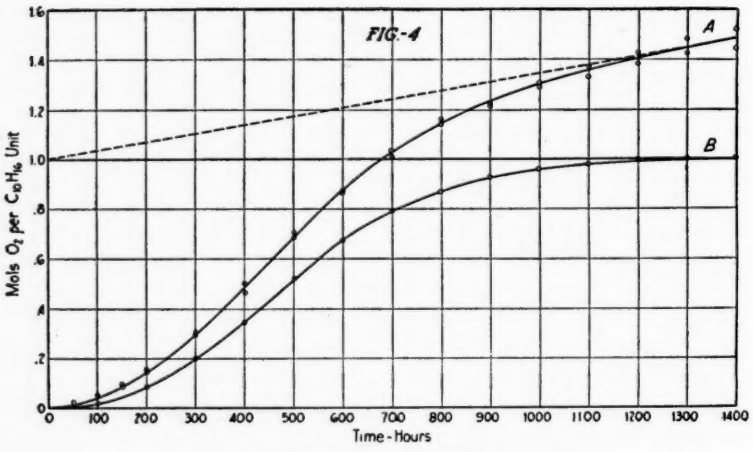
making it possible for six determinations to be made at one time. The construction of one of the systems is shown in detail in Figure 2. The sample is placed in bulb *A* attached to the apparatus by means of the ground-glass joint and mercury seal *G*. The bulb, when attached to the apparatus, is connected to the gas buret *Z* through the three-way stopcock S_3, and also to a manometer and vacuum line through the two-way stopcock S_2. The gas buret is surrounded by a water bath *H* and the sample bulb *A* immersed in a thermostat for temperature control. In

place of the usual mercury reservoir, a reservoir Y, connected to a pressure regulating cell D through the stopcock S_1, is used. This cell consists of a bulb of approximately 20-cc. volume into which are sealed two platinum electrodes N, and functions by regulated electrolytic generation of gas within it. A concentrated solution of oxalic acid is used as the electrolyte as it was found that the electrolysis of most inorganic acids and salts results in the liberation of gases which corrode and contaminate the mercury in the reservoir Y and gas buret Z. Sodium hydroxide solutions were tried but it was found that with time the platinum electrodes loosened up in the glass, probably due either to the action of alkali on glass and platinum, or to the alloying of sodium with platinum.

The manometer P is constructed so as to make possible a making and breaking of an electrical contact at the electrode F when the pressure in the system fluctuates. The double construction avoids the corrosion of contacts which would result if arcing occurred in pure oxygen. The ground-glass joint J also facilitates the adjustment of mercury levels and makes it possible to remove the manometer for cleaning and adjustment without interrupting the experiment.

Experimental Procedure

A determination is begun by pumping out the sample and buret through the stopcock S_2, the position of the mercury reservoir being so adjusted that the atmospheric pressure admitted by removing the core of the stopcock S_1 raises the level of mercury in the buret just to the stopcock S_3. When the sample has been thoroughly pumped out, as determined by noting the constancy of the mercury level in the gas buret with stopcock S_2 closed, oxygen is admitted to the buret



Reproducibility of Results
90% smoked sheet, 10% sulfur cured 2 hours
Curve B is curve A corrected for the decomposition reaction

and sample bulb through the tube O and the pressure in the system is adjusted by means of the reservoir Y to equal the atmospheric pressure when the gas buret is full. The final pressure adjustment is made by removing the removable half of the manometer and changing the position of the mercury reservoir until the mercury in both limbs of the other half of the manometer is at the same height. The removable portion of the manometer is then attached, the plug of stopcock S_1 inserted

and the gas volume, temperature, and atmospheric pressure recorded. As the sample absorbs oxygen and the pressure in the system drops, contact will be made at *F*, closing the circuit consisting of the 6-volt battery *E*, the pressure controlling cell *D*, and the mercury in the manometer. The gas pressure generated by the electrolysis of the oxalic acid solution forces the mercury up the buret until the pressure in the sample bulb *A* is atmospheric, when the circuit will be broken. It is possible to recharge the buret with oxygen as often as necessary through the tube *O* without interrupting the experiment. In case it is desired to determine the amount of oxygen physically absorbed by the sample, the gas is first measured in the gas buret before admitting it to the sample bulb. Knowing the total volume of the system makes it possible to calculate the amount of oxygen absorbed.

Experimental Data

General Nature of Results—Figures 3 and 4 show the general nature and accuracy of the results obtained. The autocatalytic nature of the reaction is plainly seen, the rate of absorption increasing rapidly during the early stages. These curves appear to be of the same type as those obtained by Eaton and Day[9] for the gain in weight of rubber during natural aging, and this similarity is regarded as evidence that the reactions occurring at 80° C. in pure oxygen are the same as those which result in natural aging. The curves as a whole can be reproduced with an accuracy considerably better than 10% as the figures indicate, but occasionally during the part of the reaction where the autocatalytic effect is greatest, duplicate samples follow slightly different curves. This is probably due to slight variations in conditions during the first part of the reaction, resulting in slight differences in rates of oxidation which persist and become greatly magnified during the remainder of the autocatalytic portion of the curves. During the later stages of the reaction these differences become smaller.

As a rule the samples absorb more oxygen than the theoretical amount necessary to saturate the double bonds. The curves tend to approach a sloping rather than a horizontal straight line, indicating that instead of approaching an equilibrium amount of oxygen absorbed, a constant rate of absorption is approached. This rate has been found to remain practically constant for more than 1000 hours at 80° C. In most cases when the straight line portion of the curve is extrapolated to the time origin it intersects the ordinate at very close to one mol of oxygen per $C_{10}H_{16}$ unit. These facts indicate that the mechanism of oxygen absorption consists of at least two separate reactions, presumably an addition to the double bonds and a breaking down of the molecule. The latter reaction continues after the first is complete and is indicated by the formation of water during the reaction. During the latter stages of the reaction this water condenses in drops on the cool parts of the apparatus and is strongly acidic. Tests for CO_2 in the system showed not more than a trace.* This is in agreement with the observations of Marzetti,[14] Dawson and Porritt,[26] and Thomson.[27] The constant rate of the reaction indicates that the curves represent only the early stages of the decomposition reaction, as it will be referred to in the following discussion, during which concentrations can be considered as remaining constant. If the final oxidation products were assumed to be CO_2 and water, 14 mols of oxygen would be consumed by each $C_{10}H_{16}$ unit. The slope of the latter part of the curves indicates that only $^1/_2$ mol of oxygen has been consumed by the decomposition reaction during 1100 hours, and since the concen-

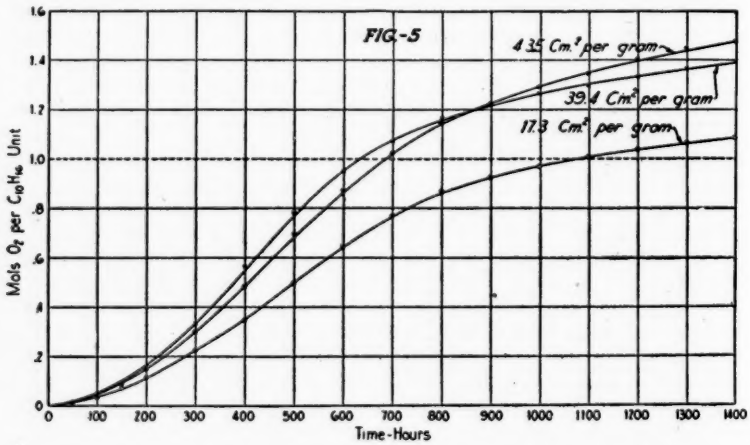
* Since completing the work here reported definite tests for CO_2 have been obtained in certain cases even during the early stages of the oxidation. Correcting for this, however, ordinarily does not greatly affect the absorption curves.

[26] *Trans. Inst. Rubber Ind.*, **2**, 345 (1927).

[27] *J. Soc. Chem. Ind.*, **4**, 710 (1885)

tration of oxygen and water in the system has been kept constant the rate of the decomposition reaction can reasonably be regarded as remaining constant throughout the first 1100 hours.

On the basis of this reasoning, a curve can be drawn representing the course of the addition reaction alone, as has been done in Figure 4, Curve *B*. Curve *A* represents both the addition and the decomposition reaction as experimentally determined and the broken line M N′ the decomposition reaction. Curve *B* was obtained by subtracting from the corresponding ordinates of Curve *A* amounts equal to the vertical elevation of the line M N′ above the horizontal line M N which intersects with M N′ at the axis of zero time. Curve *B* must, therefore, approach the horizontal line M N asymptotically, and as in this case the line represents 1 mol O_2 per $C_{10}H_{16}$ unit, the results indicate that saturation of the double bonds by oxygen occurs in agreement with the observations of Whitby[28] and of Pummerer and Burkard.[29]



Effect of Surface Area on Oxygen Absorption Compound, 90% smoked sheet, 10% sulfur cured 2 hours

During the course of the absorption the rubber first becomes tacky, then the tackiness disappears and it becomes weak and cheesy throughout. Finally, it becomes hard and brittle. At 80° C. soft rubber compounds of high rubber content were found to become tacky after absorbing from 0.02 to 0.05 mol of oxygen per $C_{10}H_{16}$ unit; the tackiness begins to disappear after approximately 0.5 mol is absorbed and the hard brittle stage is reached after approximately 1.0 mol per $C_{10}H_{16}$ unit is absorbed. At certain stages in the reaction some compounds exhibit the checking phenomenon markedly. It is felt that checking is due to oxidation of the surface to the hard and brittle stage while the inner portion of the rubber is still at an earlier stage of oxidation as suggested by King.[30] On this basis those compounds which react with oxygen very rapidly under the influence of light, and which allow oxygen to diffuse through them very slowly will surface check to the greatest extent. Under these conditions the surface will take up the oxygen before it can reach the inner portions and a hard film of oxidized rubber will form on the surface while the interior remains relatively unchanged.

[28] "Plantation Rubber and the Testing of Rubber," **1920.**

[29] *Ber.*, **55,** 3458 (1922).

[30] *Chem. Met. Eng.*, **25,** 1039 (1921).

Surface Area

It was considered advisable to investigate the effect of surface area per unit weight of sample on rates of oxygen absorption to determine whether or not rates of diffusion might be slower than the rate of combination of oxygen and rubber and thus be the controlling factor. A sheet of rubber consisting of 90% smoked sheet and 10% sulfur cured two hours at 40 pounds of steam was cut up into pieces having areas of 17.3, 39.4, and 43.5 square centimeters per gram, respectively. The absorption curves determined for these samples at 80° C. are shown in Figure 5. They show that an increase of from 17 to 40 square centimeters per gram does affect the rate of absorption but that small variations in area when it is as large as 40 square centimeters per gram are without great effect in the case studied. It is reasonable to assume that when the area per unit weight reaches a certain magnitude, rates of diffusion will be high enough to keep the rubber particles saturated throughout and will then no longer be a factor in the rate of combination of rubber and oxygen. Therefore, to make the surface area factor relatively small compared with the factors being studied, the area was always made approximately 40 square centimeters per gram.

Effect of Cure

Two important factors in curing rubber with sulfur can be reasonably distinguished; one, the combination of sulfur with rubber, and the other the action of heat apart from a change in combined sulfur content. Although these two factors were not studied separately in the experiments to be reported the results appear to show qualitatively an effect of each on rates of oxygen absorption and will be presented as additional evidence that natural aging and absorption of oxygen at 80° C. are closely related. Many more experiments are required to show definitely the relation of cure to oxygen absorption.

A compound composed of 90% smoked sheet and 10% sulfur was given cures of 2, 4, and 6 hours, respectively, at 40 pounds steam pressure resulting in sulfur combining to the extent of 1.9, 4.0, and 5.9%, respectively. The oxygen absorption curves for these cured compounds and that for raw smoked sheet are shown in Figure 6, Curves *B*, *C*, *D*, and *E*. They show that the higher the degree of cure the more rapid is the rate of absorption of oxygen within the range studied, in agreement with the observations of Marzetti,[14] Kirchhof,[31] and Stevens,[32] and also with the order of natural aging of such a series of compounds as determined by general experience. They do not agree, however, with the effect of cure on rates of oxidation as determined by Weber[33] from the acetone extract. It is suggested that the acetone extract may not be a good measure of oxidation in this case, as the difficulty of extraction probably increases with the degree of cure. It has been found that samples of vulcanized rubber which have absorbed large amounts of oxygen are only very slightly soluble in acetone.

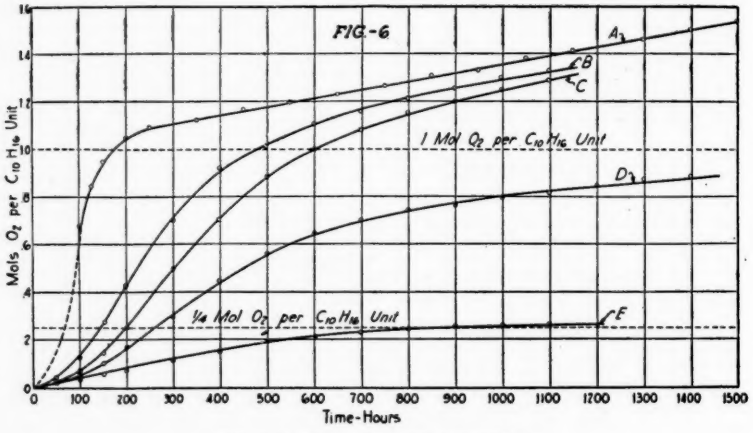
There is also shown in Figure 6, Curve *A*, representing the absorption of oxygen by a compound consisting of 95% smoked sheet and 5% sulfur which was given a cure of 5.5 hours at 50 pounds steam pressure resulting in a combined sulfur content of 4.0%. This sheet was allowed to age naturally in the laboratory for a period of 18 months before determining its rate of absorption, and because of its overcure it had aged very badly. The purpose of this experiment was first to obtain additional evidence of the relation of natural aging to oxygen absorption at 80° C., and second to determine the effect of overcure other than that due to combined sulfur.

The experimental origin of Curve *A* is the beginning of the solid line. It was

[31] *Kolloid-Z.*, **13**, 49 (1913).
[32] *J. Soc. Chem. Ind.*, **40**, 269R (1921); **37**, 305T, 340T (1918); **38**, 193T (1919).
[33] *India Rubber J.*, **25**, 639 (1903).

located with respect to the other curves by assuming that they are all members of the same family. Also, as has already been stated, the straight line portion of the curve representing the decomposition reaction usually passes through the ordinate 1.0 mol per $C_{10}H_{16}$ unit, and this straight line portion is ordinarily not reached until more than 1.0 mol per $C_{10}H_{16}$ unit has been absorbed. Since the early portion of the experimental curve lacks the upward inflection which is characteristic of freshly vulcanized rubber, as illustrated by curves *B*, *C*, and *D*, it is probable that this had occurred during the natural aging period. The complete curve as drawn represents the absorption which it is assumed would have occurred if an unaged sample had been used, the dotted portion on this basis representing the oxygen absorbed during the 18 months of natural aging.

It is to be regretted that data were not also secured for the rate of oxygen absorption of this sample when in a freshly vulcanized condition, but the apparatus had not yet been developed at that time. We hope to secure such comparative figures in the future.



Effect of Cure on Oxygen Absorption

A. 95% smoked sheet, 5% sulfur cured 5.5 hours at 50 lbs.
B. 90% smoked sheet, 20% sulfur cured 6 hours at 40 lbs.
C. 90% smoked sheet, 10% sulfur cured 4 hours at 40 lbs.
D. 90% smoked sheet, 10% sulfur cured 2 hours at 40 lbs.
E. Raw smoked sheet

If our assumptions are correct, the experimental results show that a very close relationship between natural aging and absorption of oxygen at 80° C. exists and indicate that the same reactions occur in both cases. The steepness of the early portion of the curve as compared with Curve *B* is in agreement with the bad aging qualities of compound A which, however, has a lower, combined sulfur content than B, thus illustrating the importance of overcure aside from its effect upon combined sulfur content.

It appears, as is shown by Curve *E* for raw rubber, that the type of absorption of oxygen in this case is not the same as that for vulcanized rubber. The autocatalytic effect, if present at all, is very slight and instead of taking up one mol of oxygen per $C_{10}H_{16}$ unit only $^1/_4$ mol is consumed. It has been observed by Henriques[34] that raw rubber upon being heated absorbs only traces of oxygen, and de Vries,[35] Stevens[32] and Thomson[27] state that raw rubber deteriorates very slowly as compared

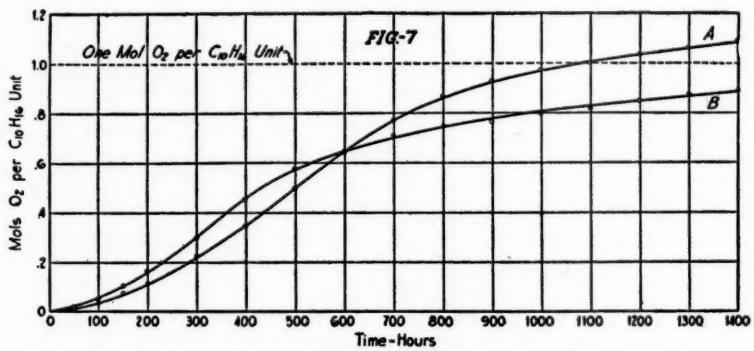
[34] *Chem.-Ztg.*, **21**, 415 (1897).
[35] *India Rubber J.*, **61**, 861 (1921),

with vulcanized rubber. Seeligmann, Torrilton, and Fauconnet,[36] however, state that raw rubber oxidized more rapidly than vulcanized rubber and Jones[37] finds that pure rubber oxidizes very rapidly.

Curve *D* for the vulcanized sample of lowest degree of cure appears to be intermediate between the type for raw rubber and that for fully cured rubber. Since this work was completed a paper by Kirchhof[38] has been published stating that the oxidation products of undercured and overcured rubber are not the same chemically or physically. These observations may possibly be interpreted to support the belief of Boggs[39] that there are three rubber-sulfur compounds formed during vulcanization which differ greatly in their stability toward oxygen. Additional support to this theory is that rubber compounds which contain a considerable amount of an anti-ager do not appear to reach the same equilibrium value as those without the anti-ager as will be shown later. Boggs maintains that anti-agers are unnecessary when the vulcanization is carried out so as to prevent the formation of the unstable rubber sulfur compound.

Effect of Over-working Rubber before Vulcanization

The curves of Figure 7 show the effect of over-working the raw rubber before vulcanization on rates of absorption. The compounds in both cases are 90% smoked sheet and 10% sulfur, but compound A was milled 20 minutes and B one



Effect of Milling before Curing on Oxygen Absorption Compound, 90% smoked sheet, 10% sulfur cured 2 hours at 40 lbs.
A. Milled 20 minutes before curing
B. Milled 1 hour before curing

hour before curing. The over-worked sample absorbs oxygen at the fastest rate during the first part of the cure, but crosses Curve *B* before saturation of the double bonds occurs. The reason for this effect is not known, but it suggests absorption of oxygen during the milling process.

Effect of Anti-Agers

The study of the effect of anti-agers was made for three purposes: first, to determine the mechanism of their action, whether it is a preferential absorption effect as some believe[40] or a negative catalytic effect; second, to obtain additional evidence

[36] "India Rubber and Gutta Percha," **1910.**
[37] *Ind. Eng. Chem.*, **17,** 871 (1925).
[38] *Kautschuk*, **1927,** 239–45, 256–61.
[39] *India Rubber World*, **76,** 79 (1927).
[40] *Rubber Age*, **20,** 27 (1926).

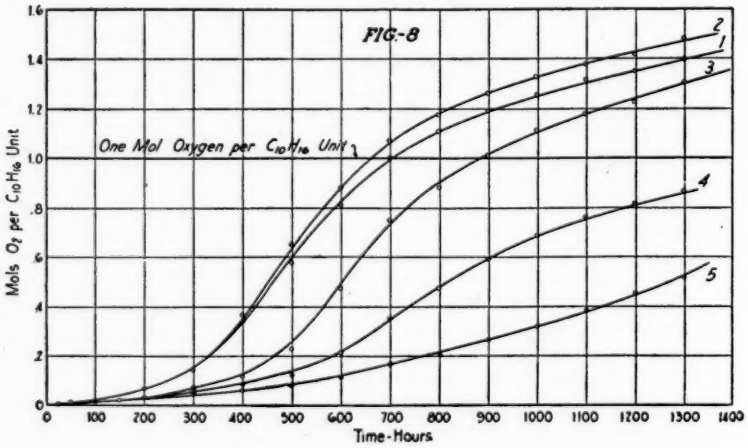
that rates of oxygen absorption are proportional to rates of natural aging; and third, to determine the relative effectiveness of various anti-agers.

The compound used for this purpose was the following:

First latex crepe	100 parts
Sulfur	2.5 parts
Mercaptobenzothiazole	0.5 parts
Zinc oxide	5.0 parts
Stearic acid	1.0 parts

To this compound were added 3 and 0.5% of two widely used anti-agers which will be designated as A and B. The absorption curves for these compounds and that for the compound without the addition of anti-agers are shown in Figure 8. They show plainly that the action of the anti-agers is not preferential absorption but negative catalysis.

It is interesting to note that a small amount (0.5%) of anti-ager A appears to accelerate rather than to retard the rate of absorption. The data indicate that



Effect of Anti-agers on Oxygen Absorption

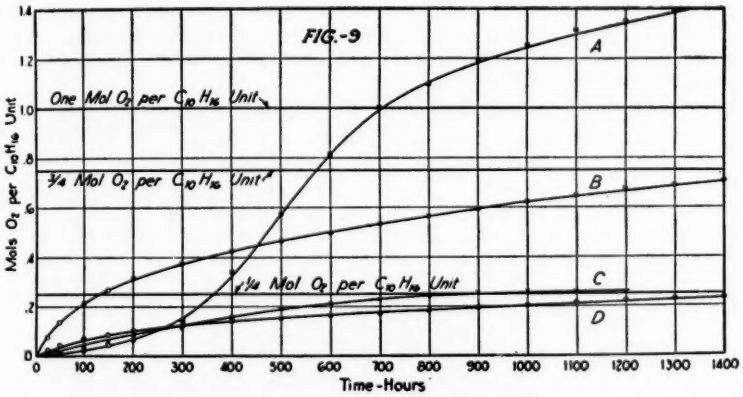
1. 0.0% anti-ager
2. 0.5% anti-ager *A*
3. 3.0% anti-ager *A*
4. 0.5% anti-ager *B*
5. 3.0% anti-ager *B*

the curves cross at about 300 hours, up to this time the rate being slightly retarded by the anti-ager, but this effect is too small to show on the curves as drawn. The accelerating action of small amounts of this particular anti-ager was at first doubted, but has been confirmed by repeating the experiment. We have been led to surmise that a reaction occurs between the anti-ager and the natural inhibitors of oxidation during the vulcanization process destroying the effectiveness of both. When sufficient anti-ager is added to react with all of the natural inhibitors, the effect of the anti-ager becomes apparent. This explanation appears reasonable because during the vulcanization of this particular compound considerable gassing occurs, indicating a reaction of some kind. The curves also indicate a considerable difference in the effectiveness of the two anti-agers. This effect of anti-agers of retarding the absorption of oxygen at 80° C. is further evidence that rates of oxygen absorption at 80° C. are related to rates of natural aging.

Effect of Ozonized Oxygen

It is well known that ozonized oxygen causes rubber to deteriorate very rapidly, but no quantitative data on rates of absorption appear to be available. The apparatus used in the previous experiments was modified by sealing in two platinum electrodes with a separation of $^1/_2$ inch approximately 8 inches above the sample. An electrical discharge in oxygen was generated between these electrodes by means of a Ford spark coil and a six-volt battery, thus producing a small concentration of ozone in the system. The sample used was the basic compound used in the investigation of anti-agers. Curve *B*, Figure 9, represents the absorption of ozonized oxygen by the compound and Curve *A* the absorption of pure oxygen.

As was expected, the rate in the case of ozonized oxygen is very much faster at first, but it rapidly decreases and soon crosses the curve for pure oxygen. There is no evidence that the reaction is autocatalytic and it appears to be of a type different from that of the oxygen reaction, as a different equilibrium value is approached. This value is not three times that for pure oxygen as would be expected if an ozonide were formed instead of an oxide, but even lower than that for pure oxygen. During



Effect of Ozonized Oxygen on Oxygen Absorption Curve

A. Absorption in pure oxygen
B. Absorption in ozonized oxygen
C. Absorption of pure oxygen by raw rubber in ozonized oxygen
D. Curve *B* replotted dividing the oxygen absorbed by 3

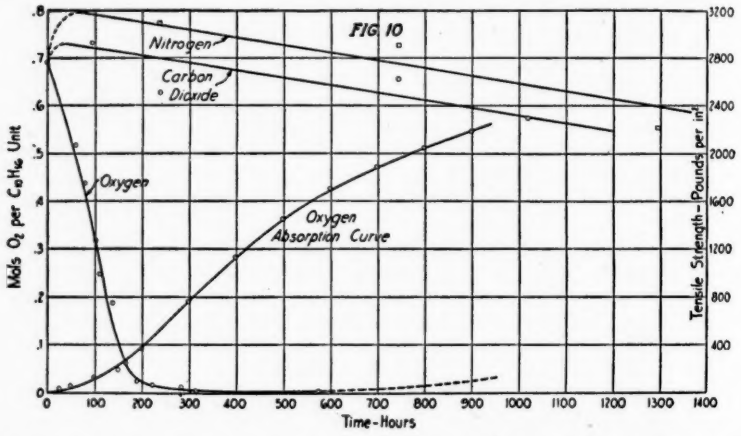
the later stages of the reaction the ozonized oxygen was replaced by pure oxygen to determine whether or not pure oxygen would be taken up as vulcanized rubber normally does, but no change in rate of absorption was noted. The results indicate that ozone causes a permanent change in the rubber, protecting it against the action of oxygen. They also suggest that the action of ozone on rubber prevents the formation or accumulation of the catalyst responsible for the autocatalytic nature of the oxygen reaction. It may even be possible to improve the aging qualities of rubber by giving it an ozone treatment. The action may be similar to that suggested by Ahrens[41] to explain the two per cent of oxygen which he claims is usually found in raw rubber. He suggests that a protective coating of oxidized rubber is formed around the latex particle which retards further oxidation. These results are similar to those published in the recent paper by Kirchhof[33] for the absorption of oxygen by rubber under the influence of ultra-violet light and suggest that the action of ultra-violet light is the production of small amounts of ozone which react with the rubber.

[41] *Chem.-Ztg.*, **36**, 505 (1912).

The appearance of the ozone curve, *B*, suggests a relationship between this curve and that for raw rubber in oxygen shown in Figure 6 and replotted in Figure 9 (Curve *C*) as approximately $^1/_4$ the amount of oxygen necessary for the formation of an ozonide was consumed and the curves have the same general shape. If the ordinates of Curve *B* be divided by 3 to allow for the difference in the amount of oxygen necessary to form an ozonide and an oxide, Curve *D* is obtained. This is not very different from Curve *C*.

The Relation between Absorption of Oxygen and Deterioration of Tensile Strength

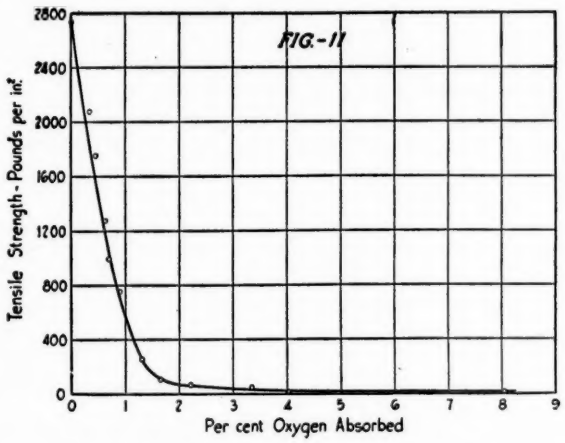
Before rates of absorption of oxygen can be used as a measure of aging qualities, the relation between the amount of oxygen absorbed and physical deterioration of the rubber must be known. To determine this, tensile strength specimens composed of the basic compound used in the study of anti-agers were placed in the bulbs of the absorption apparatus and allowed to absorb oxygen at 80° C. Periodically, several of the specimens were removed and measurements of tensile strength and elongation made on them. These measured values of tensile strength are shown



Relation of Absorbed Oxygen on Heating in Inert Gases to Deterioration of Tensile Strength

plotted against the measured amounts of oxygen absorbed by the samples in Figure 10. Along with these curves are shown curves obtained in a similar manner when the oxygen is replaced by CO_2 and by nitrogen. It was hoped that the complete tensile strength-oxygen absorption curve could be determined, but the samples which first become soft and tacky, causing them to settle out of shape in the bulbs, later became hard and stiff, making it impossible to remove them from the bulbs and make accurate measurements of tensile strength. Also, when the samples were in the soft and tacky condition they would adhere and finally form one solid mass of rubber. Rates of diffusion were then no longer fast enough to allow uniform oxidation of all of the samples. As a result, the last part of the absorption curve is not the same as that for the same compound cut up into small pieces shown in Figure 8. However, within the range of practical interest, the two curves are in good agreement. It is believed that if the samples were oxidized further the tensile strength would eventually begin to increase somewhat as shown by the dotted line as the samples undergo changes during oxidation similar to those occurring during vulcanization, with sulfur, finally becoming hard and brittle.

The effect of oxygen on tensile strength is very striking, 0.5% by weight, decreasing it by nearly 50%. Heating in CO_2 and nitrogen first results in an increase in tensile strength, probably due to additional vulcanization, and then in a very slow decrease which is insignificant compared with the effect of heating in oxygen. This decrease was greater in carbon dioxide than in nitrogen. It was observed that the samples heated in carbon dioxide changed in color uniformly throughout, from light yellow to black, indicating that carbon dioxide may react in some way with rubber at high temperatures. The results are in agreement with those of Marzetti[14] who found that less than one per cent of oxygen produces profound changes in rubber, while heating in inert gases is without appreciable effect. Jones[10] found that samples sealed up in evacuated tubes and placed in the Geer test remain unchanged after 14 days. Gorter[42] observed that rubber in sealed tubes exposed to light remains unchanged when the tubes are filled with H_2 or CO_2. Thomson[27] found that after 2.5 years in vacuum, CO_2 and hydrogen, no deterioration occurred either at room temperature or for shorter periods of time at 100° C. Tener, Smith, and Holt[3] claim, however, that very marked changes do take place in rubber when



Absorbed Oxygen Plotted against Tensile Strength

kept in evacuated tubes. It is suggested that in view of the very striking effect of oxygen on tensile strength their results may be accounted for by incomplete protection against oxygen. The tubes in which their samples were kept were closed by rubber caps through which some oxygen might diffuse and the pressure may have been as high as 5 millimeters. Also, to remove free sulfur, it was necessary to open the tubes occasionally, which would allow oxygen to be absorbed by the samples. The effect may also be due in part to further vulcanization because of the large amount of free sulfur in the samples. In the experiments here reported the tubes were evacuated with a two-stage Crowell-McNeill pump to a pressure probably not greater than 0.01 mm. for several hours. Then the tubes were closed by means of mercury seals.

The first attempt to determine the relation of oxygen absorption to change in tensile strength was interrupted by an accident after a period of 30 hours. The samples used in this experiment were somewhat undercured and the results obtained, though incomplete, are of interest. Only a slight decrease in tensile strength oc-

[42] *Caoutchouc & gutta-percha*, **12**, 8724 (1915).

cured after absorbing oxygen for 30 hours as compared with the decrease represented by the curve of Figure 10 for fully cured samples, although the rates of absorption were approximately the same in both cases. The decrease in tensile strength due to oxygen absorption was hidden by an increase resulting from further vulcanization, as was shown by the large increase in tensile strength which occurred when similar samples were heated in carbon dioxide and nitrogen. This "after-vulcanization" of undercured stock often makes it difficult to interpret the results of any accelerated aging test at high temperature which is based on changes in physical properties of rubber with time. It is believed that measurements of rates of oxygen absorption afford a means of distinguishing between undercure and good aging qualities.

If the amount of oxygen absorbed as shown in Figure 10 be plotted against the corresponding tensile strength, Figure 11 is obtained. This curve indicates first that the decrease in tensile strength of well-cured rubber can be considered as being directly proportional to the amount of oxygen absorbed, with very little error as long as the rubber possesses sufficient strength to be of practical value; and second, that the absorption curve must be determined very accurately to serve to predict the behavior of rubber over a period corresponding to its natural life.

Summary and Conclusions

In order to determine the relation between natural aging and oxygen absorption at 80° C., the effects upon oxygen absorption of a number of factors which are known to affect natural aging have been studied. An apparatus is described with which it is possible to follow the absorption of oxygen at constant pressure, temperature, etc., over long periods of time.

It has been found that the absorption of oxygen is autocatalytic in nature and appears to consist of at least two separate reactions—a decomposition and an addition reaction.

The rate of absorption of oxygen at 80° C. is dependent upon surface area when the area is small, but when it is increased to as large as 40 square centimeters per gram, small variations in surface area are without great effect, probably because under these conditions rates of diffusion are high enough to keep the rubber particles practically saturated with oxygen.

As rubber absorbs oxygen it appears to undergo changes similar to those occurring during vulcanization with sulfur. Surface checking is regarded as a preferential surface oxidation.

The mechanism of oxygen absorption appears to be different for raw rubber from that for cured rubber. Curing rubber increases both the rate and amount of oxygen absorption over that for raw rubber, and changes the character of the absorption curve. The rate of absorption increases with the degree of cure.

The action of anti-agers is one of negative catalysis rather than one of preferential absorption. The rate of oxygen absorption may be greatly retarded by their presence and their effectiveness varies with their concentration and constitution.

The type of absorption of ozonized oxygen differs markedly from that for pure oxygen. The former is taken up very much more rapidly at first, but the rate rapidly decreases and less oxygen is finally taken up than in the case of pure oxygen. The action of ozonized oxygen upon rubber appears to protect it from the action of pure oxygen. The reaction between rubber and ozonized oxygen is not autocatalytic.

The relation between absorbed oxygen and deterioration of tensile strength has been determined and it has been found that as long as well-cured rubber possesses sufficient strength to be of practical value, the deterioration can be considered

directly proportional to the amount of oxygen absorbed. Five-tenths per cent of oxygen decreases the tensile strength by nearly 50 per cent.

Heating undercured compounds in inert gases results in an increase in tensile strength at first due to a curing action, and then in a slow decrease which is insignificant as compared with the effect produced by oxygen.

The results so far obtained indicate that natural aging is essentially the result of absorption of oxygen from the atmosphere. Accordingly, it is felt that information concerning rates of absorption of oxygen will be of value in predicting the natural life of rubber compounds.

[Reprinted from the India Rubber World, Vol. 76, No. 6, pages 77–78, March 1, 1929.]

Some Practical Aspects of Rubber Evaluation

R. P. Dinsmore

Goodyear Tire & Rubber Company, Akron, Ohio

In various papers, published in the past three years, E. C. Zimmerman and the writer have made references to the variability of crude rubber as determined by the properties of vulcanized compounds of various types. We were, I believe, the first to point out the chief stumbling block in the way of establishing a standard test formula for evaluating crude rubber, namely the variation in both quality and rate of cure produced by curing the same rubber with different curing agents.

At the outset we were confronted with difficulties which resulted from a deplorable lack of standardization of rubber testing methods, and more specifically from a lack of agreement as to the proper way to select comparable cures. Indeed, it is obvious that these drawbacks have been among the major causes for lack of correlation of available data on the subject. We have stressed the importance of considering those properties of the vulcanizate which are reflected in the performance of the finished product, and have stated our objections to many of the popular criteria, such as "slope," tensile product, tensile, and coefficient of vulcanization.

We had concluded that aging should be the chief criterion of best technical cure. Accelerated age tests cannot be relied upon for comparison of different mixes, but experience has shown that for lightly loaded mixes hand tear is a reliable method of fixing the best aging cure. With this as a means of selecting the time of cure, the quality was studied by comparing the stiffness of the stress-strain curve at best cure. Later, in a paper on acceleration classification, if was shown that these conclusions might properly be modified when dealing with loaded mixes. Here the cures, as selected by hand tear and by maximum, tensile product, were in substantial agreement, except in the case of non-accelerated stocks.

Much has been written about the causes of variation of crude rubber. A great deal of this work has been done on rubber-sulfur mixes, and just how this may be translated into the terms of practical accelerated mixes is problematical. Yet we may accept the general facts that the age of the rubber tree at time of tapping, the type of soil, the nature of the season, the method and speed of coagulation, and the method of drying and sheeting, all have some influence on rubber properties. We must pass hastily over this phase of the matter, not because it is unimportant, but because, at present, we cannot expect rubber growers to furnish us with uniform rubber, when we are unable to tell them conclusively what properties we want and how to determine them. The work of the Crude Rubber Committee and The Physical Testing Committee of the Rubber Division is calculated to change this situation for the better. Just now we are concerned with asking whether the variation in crude rubber, as received at our factories, is a cause for concern and, if so, what we may do in our factory practice to offset it.

As previously mentioned, variations in both cure and quality are to be expected. Cure, however, is the more important factor. Some time ago we studied variation between bales of the same lot and finding as much variability as between lots, we checked a number of bales and found considerable variation throughout the rubber in a single bale.

In a recent test to determine the efficacy of blending, tests were made from each of a number of batches of rubber taken from the breakdown mills. In all, 48 samples, representing 48 batches, were taken over a 7-day period and were studied in a pure gum mercaptobenzothiazole friction, activated with zinc oxide, with results as follows:

	Tensile kg./cm.²		700% modulus kg./cm.²
24 Tests between.....	160–180	6 Tests between.....	140–160
15 Tests between.....	140–160	7 Tests between.....	120–140
9 Tests between.....	120–140	18 Tests between.....	100–120

This shows a rather wide variation even after blending.

Another check made to see the effect of using a high-grade tread rubber which had been tested in the friction formula above, showed these results on 20 samples.

FRICTION TEST—20 SAMPLES

Tests	700% modulus kg./cm.²
2, between.....	160–180
1, between.....	140–160
10, between.....	120–140
7, between.....	100–120

TREAD TEST—20 SAMPLES

Tests	500% modulus kg./cm.²
3, between.....	170–190
9, between.....	150–170
8, between.....	130–150

Point for point there was a general correspondence between the high and low tests for the two stocks, although there were some reversals. Here again the fluctuation is considerable. The above data are typical of a large mass which, unfortunately, time did not permit my condensing to suitable form for this hastily prepared review.

It is now pertinent to ask whether these results are reflected in any practical performance tests. Two rubbers were selected by the friction formula, giving moduli of 120 and 57, respectively. These were compounded in a solid tire stock where the differences were apparently entirely eliminated. However, on a blow-out test, the high-grade rubber gave about 45 per cent more mileage than the low grade. Two other rubbers were selected having modulus figures in the friction stock of 147 and 37. Here the solid tire stock showed about 8 per cent difference in modulus, but there was 50 per cent difference in the mileages to blow out.

In a high-grade balloon tread stock, rubbers which were selected because they gave modulus figures of 104 and 53 in the friction test gave 88 and 84 in the tread stock with abrasion loss figures of 10.9 and 11.5, respectively. The road wear resistance was in the ratio of 112 to 100.

Another test was made on a pneumatic truck tire carcass for blowout. The rubbers tested 105 and 70 modulus. On a slow speed test there was no difference beyond the experimental error. The high speed test showed a difference of 60 per cent in favor of the high-test rubber. This was on one tire for each rubber and cannot be considered as any more than indicative.

It would seem that there is enough variation of a kind which, to some degree at least, is reflected in service tests, to warrant an interest in reducing the effects in our factory stocks.

In considering the classification of rubber for factory use we have always been confronted with the problem of blending or homogenizing a sufficient quantity

to permit grading. If rubber varies from bale to bale in the same lot, we cannot be sure of the nature of any given bale unless we test it individually. The figures given for the seven-day check indicate the difficulty involved. In this case the batches were made of "pie-cut" rubber taken from four lots and ten batches were blended by taking one slab from each of ten batches and massing on the mill. Even with this procedure, the variation was so great as to be discouraging. Study of rubber variation over a prolonged period has shown that the variation is erratic; that is, the general run of rubber will come high test for a few weeks with individual fluctuations, of course, and then it may swing to an average, medium, or low test. This in itself makes lot blending ineffective.

The only reasonable alternative seems to be to mass as much rubber as is practicable on a mill or masticator and test each batch. From the results of these tests the rubber can be classified as desired, possibly into high, low, and medium classes. Compound formulas can then be made to accommodate these classes of rubber. Such a proposal requires, for many factory conditions, a rapid test. Experiments have convinced us, however, that an actual modulus test is essential. This requires sampling, compounding, curing, and testing within a very brief time. By having equipment close at hand and using short, high-temperature cures, and using cold water to condition the sheets, a single point modulus test can be obtained in less than 25 minutes after the rubber is sampled. It is thought that this is within practical working limits.

This plan is based, of course, on the assumption that a suitable test formula is available which will properly select rubber for the general run of factory stocks. As to the nature of such a formula, I believe it must be largely determined for the individual case. Certainly our experience would indicate that it would not do to test with one accelerator and compound with another. I must confess to being somewhat disconcerted by the service results, particularly of the solid tire stock. It must be borne in mind that the number of service tests was limited.

It is not intended that any one should conclude that physical tests made upon a lightly loaded mix are more significant as to ultimate service than tests on the actual compounds. It may eventually prove that certain properties resulting from the original crude rubber are masked by compounding so that they are difficult to uncover in our present laboratory tests and are better indicated by the pure gum stock. Certainly we must view with caution the opinion that identity in laboratory tests such as stress-strain, resilience, and abrasion, necessarily insures identity of service performance. As we refine our laboratory practice and correlate it more exactly with service results, we shall throw more light on this interesting subject.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 4, No. 5, pages 396–411. February, 1929.]

Pigment Reinforcement

R. W. Lunn

INTRODUCTION—This paper considers the reinforcement of rubber by various agents, but the point of view is taken from a rather new position. As a result the familiar conclusions are reached, but the new aspect has some points of interest.

The first thing is to define the meaning of the term "reinforcement," and for the purpose of this paper it is used to indicate energy. The extension of rubber and its compounds involves the input of energy, which increases continuously to a maximum at which breakdown occurs. This paper is a consideration of the energy relationships between rubber and pigment under extension.

A familiar way of comparing the reinforcing powers of rubber pigments is to compare the total energies of resilience of the compounds containing the pigments. Pigments are compared on a basis of equal volumes. The resilient energy figures compared are those of the whole compound. For the purpose of this investigation an attempt is made to analyze the total energy value and assign a certain proportion of it to the rubber and the remainder to the pigment. However, it must not be understood that the pigment as such has an energy value like rubber. The addition of pigment causes an energy change in the rubber compound which can be associated with that pigment.

To make the idea clearer it may be useful to express it in an elementary mathematical form.

Consider a rubber compound containing ingredient "A." A definite volume x of the pigment is used in the compound with 100 volumes of rubber.

Let E_A represent the total energy of the compound containing "A;" e_R represent the energy due to the rubber portion; and e_A represent the energy assigned to the x volumes of pigment "A" then $E_A = e_R + e_A$. Hence e_A/x is the energy assigned to a unit volume of the pigment under the conditions of the experiment. This value is characteristic of the pigment under definite conditions.

The experiments were carried out with the object of determining e_A/x at various concentrations of pigment and at various extensions up to the breaking point.

It was considered essential that this investigation should include a consideration of energy values at extensions below the breaking point.

It seems very easy to assume in the figures for the ultimate breaking stress and ultimate elongation, a degree of accuracy which is both fictitious and misleading. The point will be dealt with, however, in describing the experiments.

In order to consider energy values at extensions below that of the breaking point, it is necessary to make some assumptions before even an elementary mathematical treatment can be attempted. For the purpose of this paper, what appears to be the simplest possible visualization is taken. Other treatments are possible. Grave objections against the present proposition can be raised and this fact should be clearly recognized.

The ideal base upon which to start work would be capable of acquiring the properties of vulcanized rubber without the complication of adding the agents by which the state of vulcanization is achieved. Of course this is impossible. The base must contain vulcanizing agents but since they must remain constant in relation to the rubber the correction involved in making allowance for their presence is comparatively simple.

Suppose that one cubic inch of rubber is taken and to it is added an amount of pigment in the ratio of x volumes of pigment to 100 volumes of rubber. The original one cubic inch of rubber becomes a cube of rubber containing $\left(1 + \frac{x}{100}\right)$ cubic inches.

The question now to be answered is—At what elongation of the compound has the rubber in the compound been extended, say 100 per cent, 200 per cent; and so on, corresponding to 100 per cent, 200 per cent elongation of the all-rubber cube?

It is assumed that on adding pigment to the rubber in the ratio of x volumes of pigment to 100 volumes of rubber, the size of the cube increases but the pigment concentrates at one end of the cube. (See Figure 1.) When this compound cube is extended, the rubber extends and the pigment extends in the same degree. That is, an increase of, say, 100 per cent in the elongation of the cube is achieved by an elongation of 100 per cent on the part of each constituent of the cube. The percentage increase in the elongation of the rubber portion of the cube is the same as the percentage increase in elongation of the compound, so that when the cube as a whole

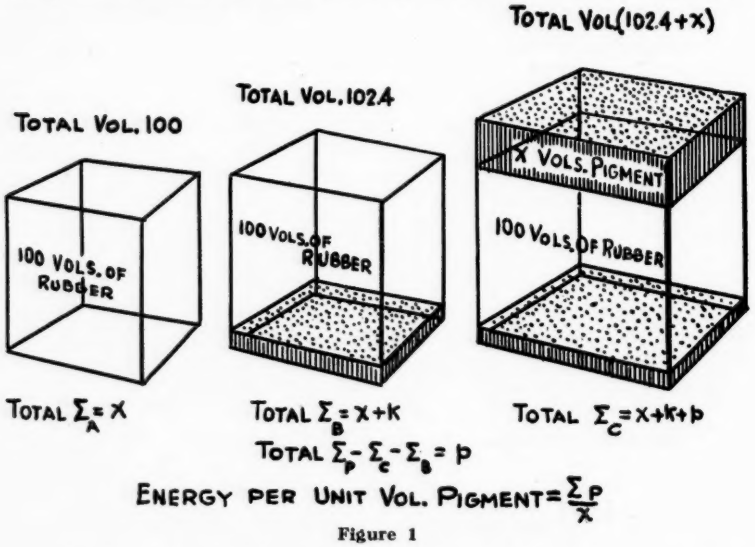


Figure 1

elongates 100 per cent the rubber portion of the cube also elongates 100 per cent, and so on up to the point of rupture. There are objections to this simple treatment but it is not proposed to discuss them here.

It now becomes easy to assign even at any elongation up to the break an energy value to the pigment portion of various compounds separate from the energy value of the rubber portion of the compound.

The Experiments—An examination of the reinforcing properties of four substances used in rubber compounding will be considered. Barytes is taken as representing the lower end of the scale at which reinforcement is generally assumed to be almost absent. The barytes used was precipitated barytes. Zinc oxide is taken as a somewhat obsolete but definite reinforcing agent. A soft black, "thermatomic" black in this case, is taken as representing what is the modern reinforcing agent similar in type to zinc oxide in giving reinforcement without marked stiffening, and gas black is taken as the material at the highest point of the scale, giving, according to general ideas, the maximum reinforcement.

In carrying out the experimental portion of the program, deviations were made from the usual paths to rather a marked extent, and these differences must be dealt with as if a comparison is made between the results obtained in these experiments and those of other observers these deviations may be important. In the organization of the work, there were two conflicting ideals to be considered. In the first place, standard experimental conditions were required, and in the second place, it appeared desirable to use compounds reasonably similar to those used in ordinary factory practice.

The two ideals are not quite parallel, and an indication must be given of how a compromise was made between them. The first point took into account the structure of the rubber itself. Rubber is assumed to have a two-phase structure, and in the process of mastication, the structural units of the rubber are broken down according to this visualization and join the fluid phase. This breaking down is not complete but is progressive according to the amount of mastication to which the rubber is submitted, and is marked by an increasing plasticity and by a progressively decreasing viscosity in solution.

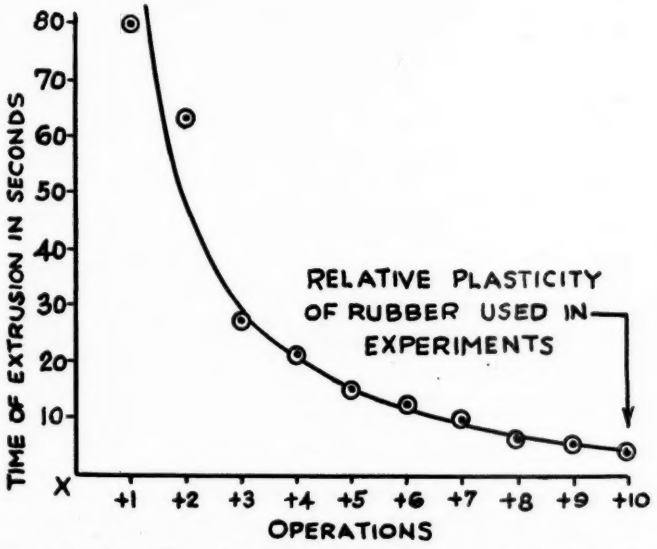


Figure 2—Relative Plasticity of Rubber during Preparation for Use in Base

The incorporation of the ingredients of the compounds used in the experiments necessitated widely varying amounts of milling so that the mastication of the rubber during the mixing process was likely to be a highly variable factor. On this account the rubber taken for the base was masticated much more severely than is done in ordinary mill room practice by treating for very short periods on a cold mill. This, of course, is a marked deviation from ordinary factory practice.

The extent to which this mastication was carried is indicated in a curve (Figure 2) showing the effect of each of the later operations on the plasticity of the rubber. To give a comparative idea it may be pointed out that while a standard factory batch has a plasticity figure of 250, this batch was masticated to give a figure of 80 before any special measurements were made. The plasticity figures then fell until finally a figure of approximately 4 was reached, and in this condition the rubber was used in the various experiments. The work was carried out in the mill room on

a batch of rubber big enough for the experimental requirements and the curve indicates a very fair regularity for a series of operations of this kind. It will be noticed that the curve is plotted showing operations against plasticity. It would be clearly incorrect to suggest that further mastication would cause no further reduction in plasticity. It was assumed, however, that at this point the further mastication due to milling during mixing would have relatively little bearing on the results. It may be interesting to note that the acetone extract of the rubber at the end of the mastication was 3.24 per cent.

Having obtained a batch of crude rubber which had been masticated to almost a "flat" plasticity, a "flat curing" base was needed upon which to compound.

The development of a flat curing compound involved the use of an accelerator but, since the substances to be examined were possibly active in relation to organic accelerators, obviously the accelerator could not be an organic one. Various carbon

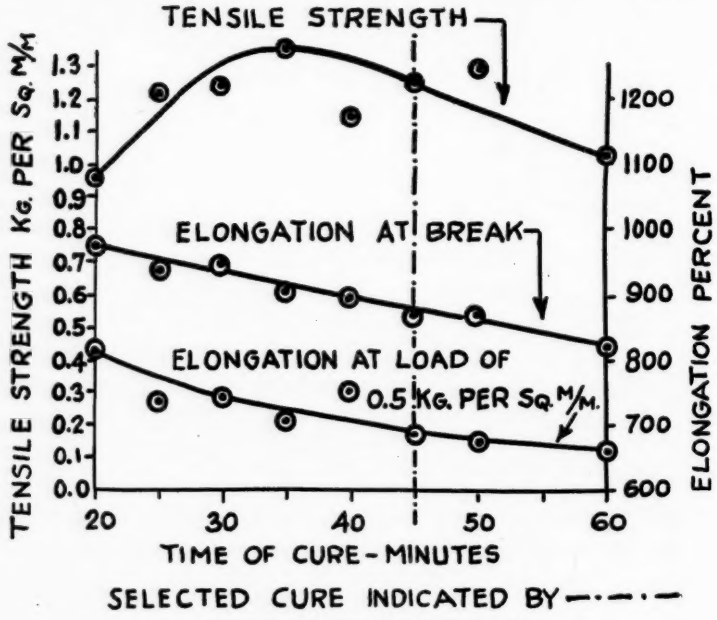


Figure 3—Data on Base Compound

blacks, clays, and zinc oxide influence in a marked degree the activity of organic accelerators. As a result reliance had to be placed on litharge. It will be remembered that Wiegand used a litharge base in his work on reinforcement. He used 30 parts by weight of litharge in 100 parts by weight of rubber. His base compound might have been used for this set of experiments but the high proportion of litharge was viewed unfavorably. A high proportion is rarely used in actual practice, and so a compound was employed containing a much lower proportion, but which would still give a "flat cure." The degree to which this was successful is indicated by the figures.

The base compound consisted of: rubber, 100 parts by weight; litharge, 10.3 parts by weight; and sulfur, 3 parts by weight.

This base will be recognized as being quite a familiar one in any general rubber factory. The litharge may appear to be an extravagance in these days of organic

accelerators, but it does represent a base upon which very useful and practical compounds can be built. It is also quite incapable of reaching the "optimum" cure so frequently used in experimental rubber work. At the optimum cure the highest possible tensile strength is developed without consideration for any other property. No one, however, cures to the optimum for factory production, and since this paper is not essentially concerned with optimum figures or with limiting figures, one of the ideals was satisfied by adopting this compound as a base.

The preliminary work simply consisted in vulcanizing at various times at a steam pressure of 40 lb. per square inch and examining the stiffness and the ultimate

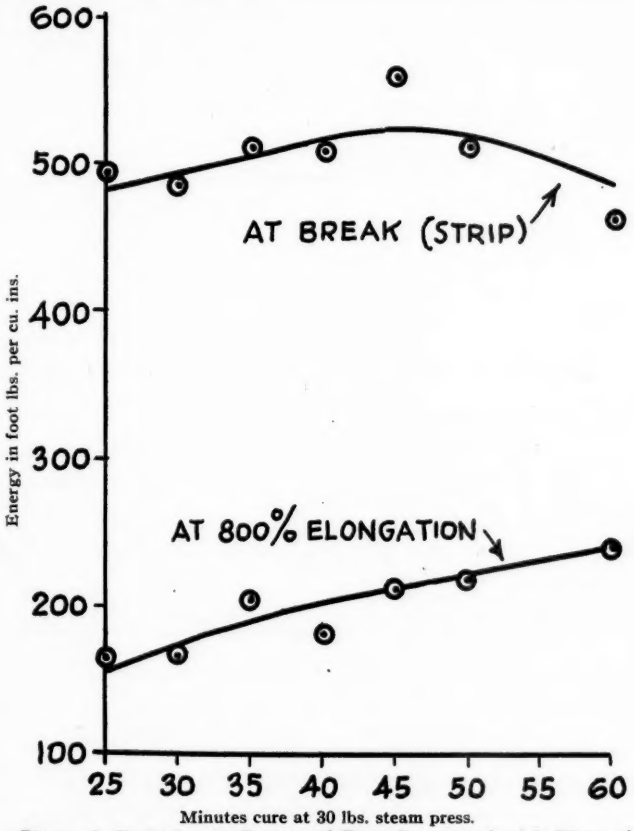


Figure 4—Variation in Energy of Base Compound with Time of Vulcanization

tensile strength of the samples. This indicated that probably a suitable flat range could be obtained.

The next step was to lengthen the time range by reducing the vulcanizing steam pressure to 30 lb. per square inch and to prepare test pieces under these conditions. These were examined for ultimate tensile strength, elongation at break, and stiffness, and the results indicated in Figure 3. It must be pointed out that up to this point all the results—including, of course, the ultimate strength—were determined on Schopper rings. At this stage it became fairly evident that a suitable time of cure would be found in the region of 45 minutes at 30 lb. steam pressure.

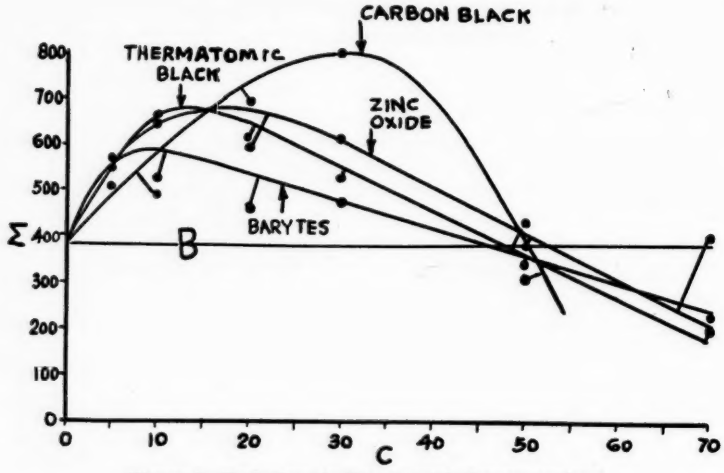
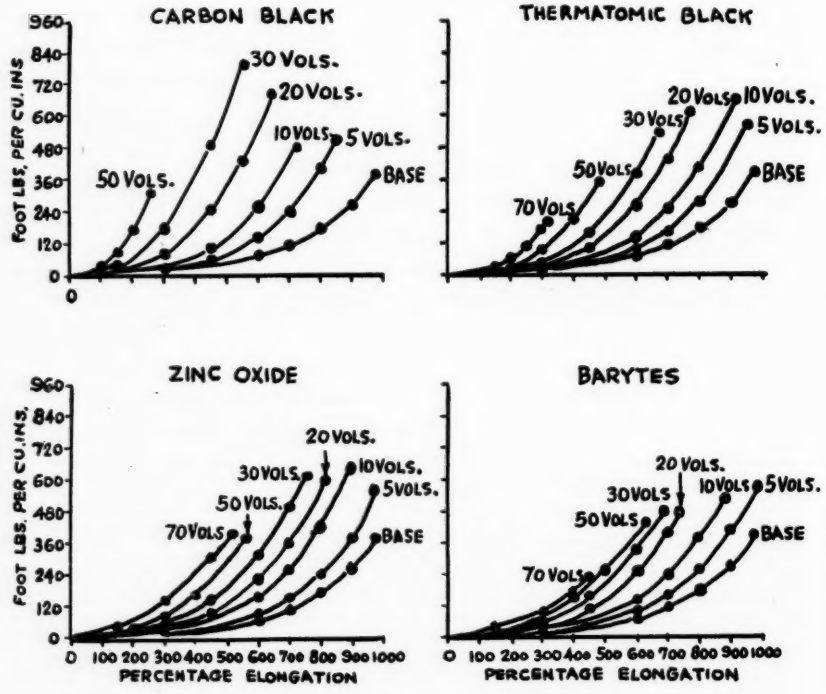


Figure 5—Variations in Energy with Concentration



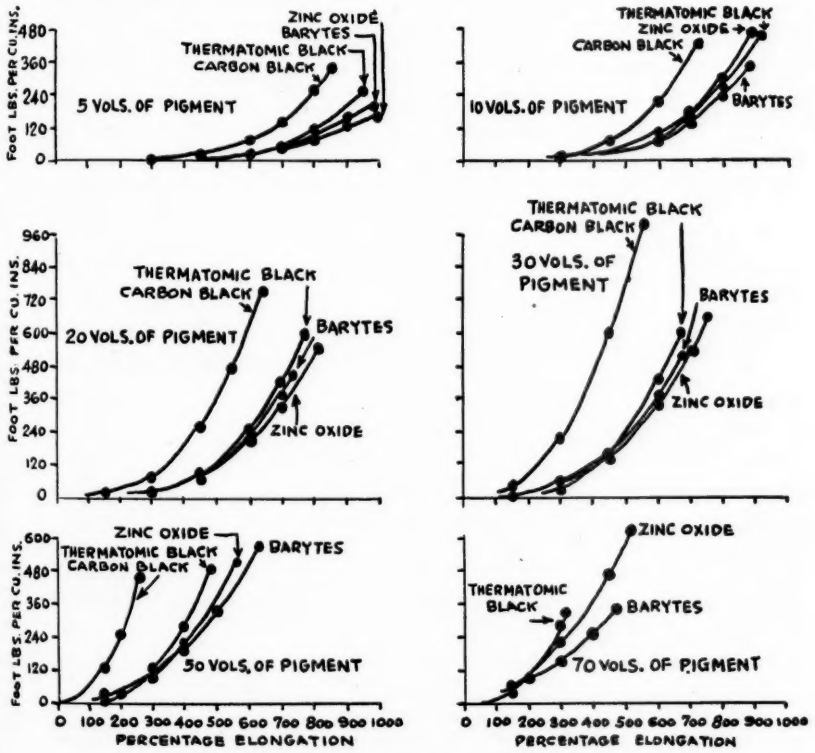
TOTAL ENERGY-ELONGATION CURVES

Figure 6

The final step was to consider the energy values of the base compound cured at various times over a comparatively short range. These energy values were determined in a manner described later. The energy values are shown in Figure 4 at an elongation of 800 per cent and at the ultimate elongation.

The curves were taken as evidence that a standard curing time of 45 minutes at 30 lb. steam pressure introduced no predominant errors.

None of the materials examined was marked by a tendency to accelerate or to retard a base stock of the type used, so that their influence in this connection was assumed to be neligible.



TOTAL PIGMENT ENERGY—ELONGATION CURVES

Figure 7

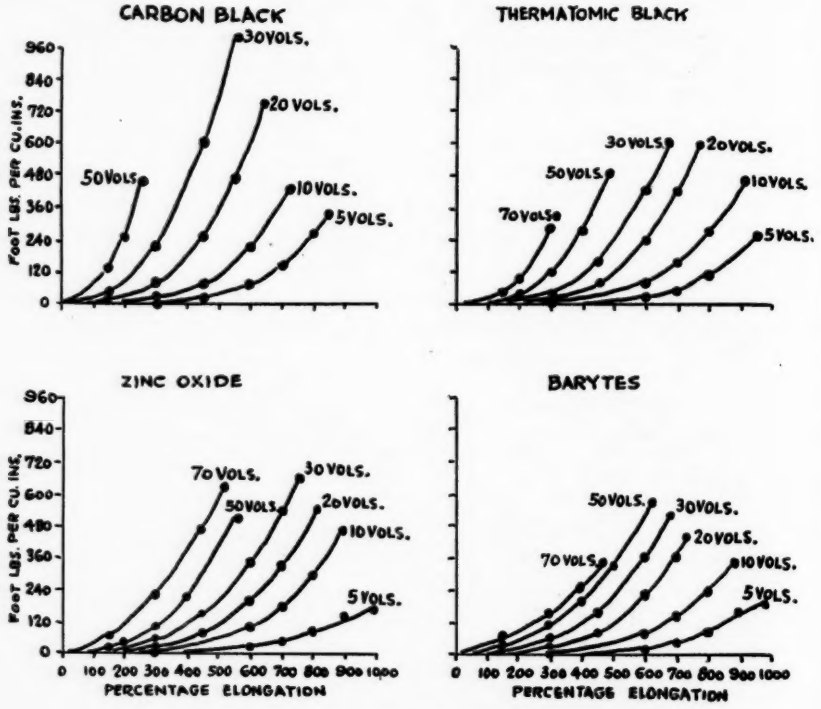
The energy determinations in this paper were made on the stress-strain curve drawn by the autographic Schopper machine, but the curve obtained in this way with the Schopper ring test piece was not considered the best means of determining the end point, particularly with highly loaded compounds.

The ring is a comparatively large test piece, and the chance of a break occurring owing to a fault is proportional to the bulk of the test piece. Any ultimate figure for the breaking tensile strength is thus likely to be low. For this reason the determination of the end point for a straight test piece of approximately $^1/_{10}$ of an inch cross section was adopted. The shoulders of the test piece were wide so that gripping was easy. If the break occurred outside the $^1/_{10}$ of an inch cross-section length, the results were rejected. No difficulty was found in obtaining a series of

figures for the breaking stress which fell reasonably close together. The end points were always considerably ahead of the Schopper end points and so the Schopper curve was taken and extended to the higher end point. This curve was accepted as the true curve. Four points should be noticed in favor of this procedure.

In the first place, consider the size of the Schopper ring. Its size tends to provide the opportunity for an accidental break due to some physical imperfection. The ideal test piece has no physical imperfections, and since this is so, one might certainly suggest that its size tends toward zero.

The second point is that some of the compounds planned for the experiments were very heavily compounded and the risk of breaks through mechanical faults was proportionally increased.



TOTAL PIGMENT ENERGY-ELONGATION CURVES

Figure 8

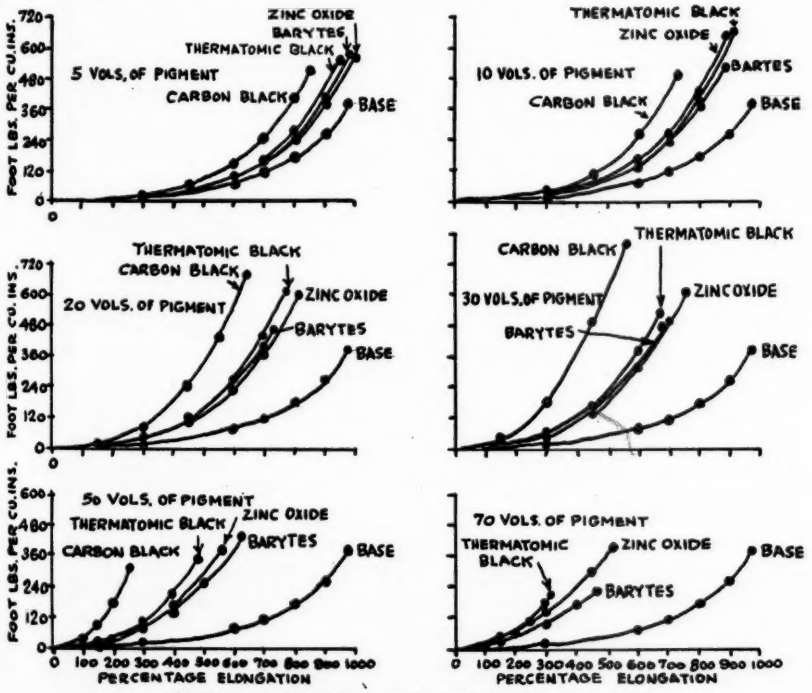
The third point is a plea of moderate justification because when the curves are examined it will probably be agreed that the end points appear to be related in quite a reasonable fashion.

The fourth point is that the conclusions reached in this paper are independent of the breaking values and thus the end points determined in the above fashion may be ignored entirely. The curves themselves will be interpreted and no effort will be made to stress unduly the weight of any evidence which depends upon breaking values.

The Results—The results of the work are summarized in the form of curves. The most familiar way of showing the reinforcing properties of pigment is to

exhibit them in the form of energy-concentration curves. The ultimate energy value of the total compound is employed, and an opinion has already been expressed that the degree of accuracy assumed in these values may be misleading. The general conclusions to be drawn from the curves are perfectly clear, but no high degree of accuracy should be assumed.

Figure 5 shows energy-concentration curves, and with the exception of that for barytes they are not notably different from similar results obtained by other observers. Carbon black, when added to the base caused an increase in the total energy of the compound until a high concentration was reached. Zinc oxide and "thermatomic" black behaved in a closely similar manner to one another. The position of the curve for barytes is interesting. It must be noted, however, that



TOTAL ENERGY-ELONGATION CURVES

Figure 9

this barytes was precipitated barytes. Barytes is usually regarded as a diluent, but in this case it definitely acted as a reinforcing agent until a loading of between 50 volumes and 70 volumes was reached. It may be emphasized that the energy values depend only upon breaking values. Apart from the objection to end points on the score of accuracy, the energy properties of compounds within the limits of extension are valuable indices of the values of the compounds in practice.

On this account Figure 6 shows resilient energy at various elongations up to break plotted against elongation. These curves have been derived by taking the stress-strain diagram and determining the energy input at elongations below the breaking point. It will be noticed that the curve for the base compound is included in the group.

The next set of curves (Figure 7) shows the same curves as in Figure 6, but the curves for the same volumes of the pigments are grouped together. As the pigment concentration increases, the curves separate more and more from that of the base compound. The outstanding reinforcement due to gas black is very evident.

The curves for zinc oxide and "thermatomic" black are so closely associated that they might be considered identical, although a difference appeared later. The curious feature again appeared in the precipitated barytes curves. Up to a concentration of 50 volumes, the behavior of the barytes compounds was very similar to that of the corresponding "thermatomic" black and zinc oxide compounds at elongations below the point at break. It is clear on the whole, of course, that the end point was reached at an earlier stage than in the other two cases, but at any elongation below the point of rupture the energy input in the three cases was substantially the same. By reference to the cube visualization it will be seen that two

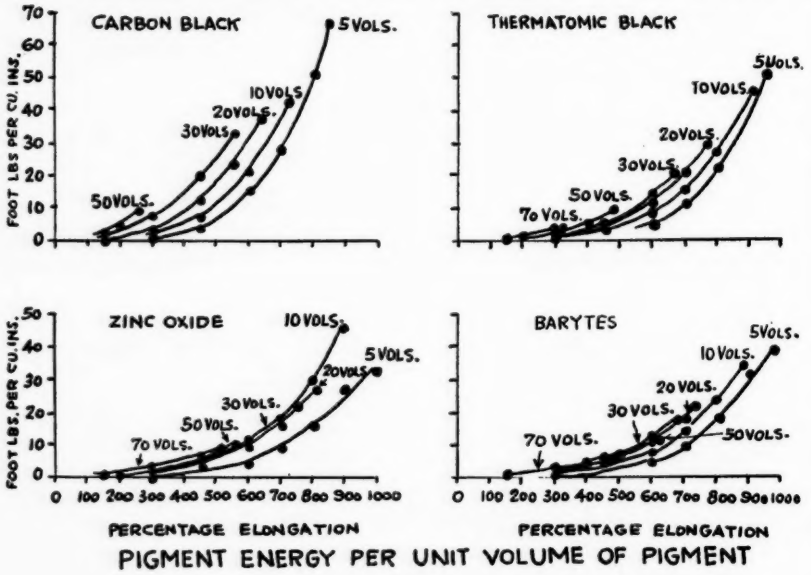


Figure 10

of the quantities expressed in these diagrams, which were required before pigment reinforcement can be estimated, have now been derived.

In the base curves is found the energy per cubic inch of the base compound, that is, Σ_B and in the various curves for the compound is found the energy per cubic inch of the compounds. By the application of a simple factor to correct for volume so that each compound contains one cubic inch of rubber the value Σ_C in our mathematical expression is obtained.

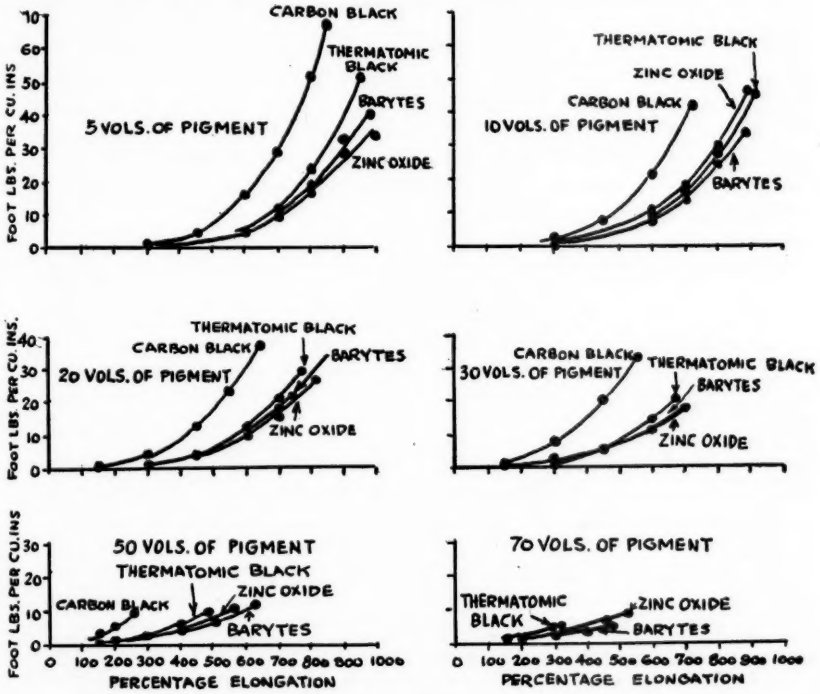
The difference between these two values gives a measure of the energy change due to the pigment. These values have been expressed in Figures 8 and 9. These are very similar curves to those showing total energy-elongation relationships. They indicate the value Σ_P in the mathematical expression. (See Figure 1.)

The final stage was to determine the values associated with unit volumes of pigment under various conditions—that is $\frac{\Sigma_P}{x}$.

A consideration of the group of curves (see Figures 10 and 11) shows that in no

case was there a sharp change in the mechanism of reinforcement. The ultimate reinforcement per unit volume declined progressively as the concentration increased. Up to the concentrations used in these experiments, there was no evidence of a sharp end point to reinforcement at which agglomeration of pigment occurred and simple dilution took place. In all cases the pigment was adding definitely to the energy of the compound under elongation.

It is now quite clear, however, that the two blacks were behaving in a manner different from zinc oxide and barytes. It will be noticed that the curves for the blacks are separated from one another quite distinctly.



PIGMENT ENERGY PER UNIT VOLUME OF PIGMENT

Figure 11

The zinc oxide curves from the 10-volume concentration lay very close together, while the barytes curves from the 20-volume concentration upward lay so close together that they were difficult to distinguish in the figure.

In the case of both blacks the reinforcement per unit volume at any particular elongation increased as the concentration of the pigment increased. The effect was more marked in the case of gas black than in the case of the thermatomic black.

The reinforcement per unit volume by the zinc oxide appeared to increase in a much less marked degree as the concentration increases above 10 volumes, but in the case of barytes the reinforcement per unit volume appeared to reach an approximately constant value for each elongation when the concentration exceeded 20 volumes. It has been pointed out already that by using precipitated barytes the results certainly differed, probably on account of particle size, from what might have been anticipated.

It appears probable that some fillers, perhaps natural barytes, for instance, might show that with decreasing concentrations the energy values per unit volume of pigment increased, that is, that with increasing concentrations the curves would begin to fall below one another.

The curves (Figures 10 and 11) indicate what may be termed the *specific reinforcing power of the pigments* examined under a variety of conditions of concentration and elongation. The increases of concentration and elongation caused a progressive increase in specific reinforcing power in the cases of the two blacks. The zinc oxide showed the same tendency to a smaller degree, but in the case of barytes the specific reinforcing power appeared to reach a constant value for each concentration and elongation.

It is likely that some pigments will show a progressively decreasing reinforcing power as the concentration of the pigment increases beyond a certain critical point.

The last group of curves (Figure 12) summarizes the ultimate energy values in the form of energy per unit volume concentration. It should be noted that the determination of the curves involved the breaking values.

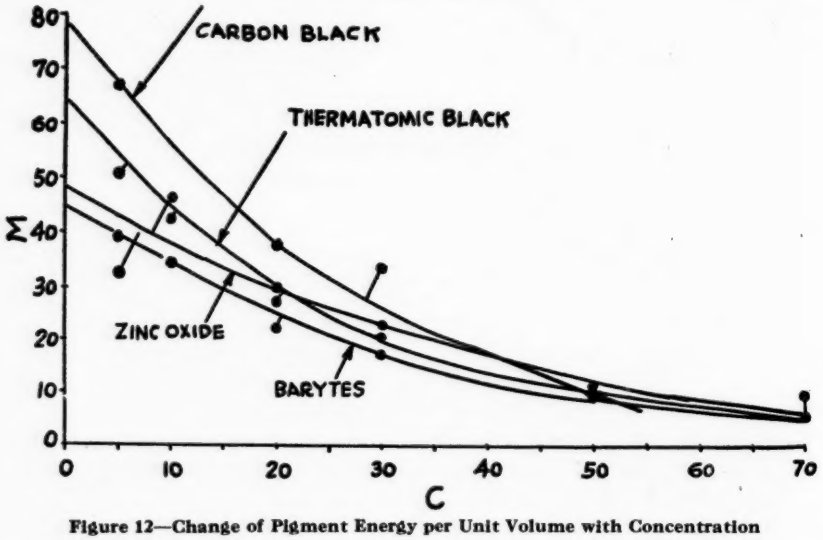


Figure 12—Change of Pigment Energy per Unit Volume with Concentration

Two interesting suggestions may be made. All the curves tend toward zero energy as the concentration increases. This appears to suggest that under conditions showing the lowest reinforcing value the pigment energy will not fall below zero. It may reach zero, in which case the pigment will act as a simple diluent, but it does not appear likely that it can effect a negative reinforcement, that is, it can reduce the amount of energy associated with the rubber portion of the compound. It will be noticed also that the curves tend to run close together from the 50-volume concentration upwards. This seems to indicate that at high concentrations no pigment is likely to show any notable advantage from the point of view of its energy properties over any other pigment. This observation may be of considerable practical interest.

In conclusion it is necessary to emphasize that the values given in this paper must be interpreted in accordance with their method of determination.

It is intended to extend the investigations outlined in the above paper.

[Reprinted from the Journal of the Society of Chemical Industry, Vol. 48, No. 10, pages 55-59T, March 8, 1929.]

The Nature of Vulcanization

Part IV

H. P. Stevens and W. H. Stevens

The Limiting Figure for Combined Sulfur

The experiments of Spence and Young[1] showed that the maximum amount of sulfur capable of combining with rubber was in the neighborhood of 33% of the vulcanized product. This was a little higher than that called for by the formula C_5H_8S, which required 32%, or a vulcanization coefficient of 47. The difference may be attributed to a combination of sulfur with protein and resin constituents. Subsequently, the experiments of Skellon[2] indicated that with a sufficient excess of sulfur, namely, 66.7% on the rubber, vulcanization coefficients exceeding 50 were obtainable. The whole subject is clearly set out under the heading "Remarks on the nature of vulcanization processes" on p. 239 on Part VII of Communications of the Netherland Government Institute for Advising the Rubber Trade and Rubber Industry, published in 1916.[3]

The high figures obtained by Skellon may be attributed to the prolonged heating at high temperatures (9 hrs. at 140°), causing a partial breaking down of the rubber molecule, so that the sulfur additive products formed do not entirely consist of rubber molecules saturated with sulfur, but in part at least of sulfur derivatives of decomposition products.

The experiments of Spence and Young were criticized on the ground that the proportion of sulfur used was very little more than that required for saturation.

More recently, in a varied series of experiments, Whitby[4] has shown that hot vulcanization in solution yields products containing not more than 32.4% of combined sulfur, although the proportion of sulfur used amounted to ten times the weight of rubber, thus providing a large excess of sulfur over that required for saturation.

Since 1916 the development of the so-called super-accelerators has enabled soft vulcanized rubber to be prepared by heating for short periods at 100° or even lower temperatures. Such accelerators have not been found of much use in the manufacture of vulcanite, probably because they are unstable at the high temperatures usually employed, so that if used in vulcanite mixings they only function in the earlier part of the "rise." We have found, however, that given a sufficiently long period of heating at low temperatures vulcanite can be advantageously prepared with the aid of super-accelerators.[5] At temperatures at or below 100° decomposition or degradation of the rubber molecule is improbable, and it occurred to us that a series of vulcanites prepared in this way would yield interesting data in regard to limiting figures for combined sulfur. As is well known, most super-accelerators do not develop their maximum activity except in the presence of substantial quantities of zinc oxide, and consequently to obtain optimum conditions it is necessary to include this activator in the vulcanite mix. As, however, results can be obtained in the absence of zinc oxide where the accelerator consists of a zinc salt, experiments

[1] *Kolloid-Z.*, **11**, 28 (1912); **13**, 265 (1913).
[2] *Rubber Industry* (London), **1914**, 172; *Kolloid-Z.*, **14**, 96 (1914).
[3] See also Weil, *Kolloid-Z.*, **31**, 303 (1922).
[4] Whitby and Jane, *Trans. Roy. Soc., Canada*, **20**, 121 (1926).
[5] British Patent 269,693.

were also made with such salts, although the conditions are less favorable for exhaustive vulcanization.

The various super-accelerators are not equally suitable for vulcanite mixes. After preliminary trials the zinc salt of diethyldithiocarbamic acid was chosen so that parallel experiments could be included in which no zinc oxide was used.

Zinc diethyldithiocarbamate may undergo some decomposition during vulcanization. If undecomposed the accelerator will be extracted by the acetone when the vulcanite is analyzed, and the sulfur it contains will be included in the free sulfur. If decomposed it is almost certain that the zinc will be converted into zinc sulfide, and such sulfur would be reckoned as if combined with the rubber.

In most of the experiments recorded below, the specimens were extracted with a mixture of hydrochloric acid and ether[6] to decompose the zinc sulfide present, but in any case the amount of sulfide sulfur formed is relatively small, even when the proportion of accelerator is high. Thus, with 5% of accelerator on the rubber, the amount of zinc sulfide formed would amount to 0.36% calculated as combined sulfur or with 20% of accelerator it would similarly amount to only 1.43%.

With regard to any unchanged accelerator extracted with acetone, this has no influence on our results, as the combined sulfur in all cases was determined directly by analysis of the extracted rubber and not by difference from the free sulfur extracted with acetone. It is also possible that zinc oxide may react with sulfur forming zinc sulfide during vulcanization. This is unlikely, as only traces are formed in the absence of accelerators, although the temperatures employed are substantially higher.

It will, however, be seen from the figures (in certain cases) that, assuming the whole of the zinc present to be converted into zinc sulfide and allowance made for this in calculating the coefficients, the figures thus obtained are still considerably in excess of those required for the formula C_5H_8S. Thus, for example, in series I, compound No. 7, the sample vulcanized for 168 hrs. at 100° yields on analysis a coefficient of 145.9 whereas the coefficient given by the compound C_5H_8S supplemented by the sulfur derived from all the zinc as zinc sulfide would be 56.3. The maximum coefficient obtained for the same specimen after exhaustive extractions with acetone and ether-hydrochloric acid mixture was 72.5, so that a large part of the combined sulfur complex is decomposed by this treatment.

Experiments were also made following Whitby's method,[7] that is, heating the rubber and vulcanizing agents in solution in a common solvent, a mixture of *o*- and *p*-dichlorobenzene, which is liquid at normal temperatures. Some mixes were employed using our own formulas and others having the large excess of sulfur (1000%) used by Whitby. The maximum coefficient obtained by this method was approximately 61.

Further experiments were made employing a "sprayed" rubber and a specially purified sample which contained considerably less nitrogenous substance than normal crepe,[8] together with a crepe control. They were vulcanized at a low temperature (70°) and analyzed for the combined sulfur. Whitby concluded[7] that the absence of the ordinary non-rubber constituents was without influence on the end point of the reaction, and so far as our experiments go they bear out his conclusion. We found the coefficients of our three vulcanites to be in close agreement after allowing for the non-rubber constituents.

Finally we endeavored to isolate and examine any rubber-sulfur degradation compounds which may have been formed during vulcanization. As already stated,

[6] *Analyst*, **40**, 275 (1915).

[7] Whitby and Jane, *loc. cit.*

[8] de Vries, *Arch. Rubbercultuur*, **12**, 559 (1928).

the apparently exceptional figures obtained by Skellon may be attributed to the degradation of the rubber molecule due to the long period of heating at a comparatively high temperature. The acetone extracts of these rubbers may have contained sulfur derivatives of degradation products. Even soft vulcanized rubber when degraded is to some extent soluble in acetone.[9] Therefore it was decided to carry out an extensive acetone extraction of a "low-temperature" vulcanite together with an extraction of a similar material vulcanized in the normal way at a high temperature, and to make an examination of the extracts obtained.

In brief it appears the degradation products containing combined sulfur are not formed under the conditions examined. That is to say, the brown coloring matter associated with the acetone extract, which can be removed from the crystalline sulfur forming the bulk of the extract, and which it was thought might consist of degradation products, does not appear to contain sulfur compounds, but presumably consists of decomposition products derived from non-rubber constituents. Furthermore, the continuation of the extractions over several months showed that the vulcanites continued to yield very small quantities of free sulfur to acetone as long as the extraction was continued.

Experiments with "Low Temperature" Vulcanites

A mixture of different samples of best quality pale crepe plantation rubber was milled in the ordinary way and mixed with the required amount of sulfur. A portion of the rubber was set aside and into this was milled the zinc oxide and accelerator. The two doughs were then subsequently mixed in the correct proportions to give the mixes detailed below, which were then sheeted about $^3/_{32}$ in. thick.

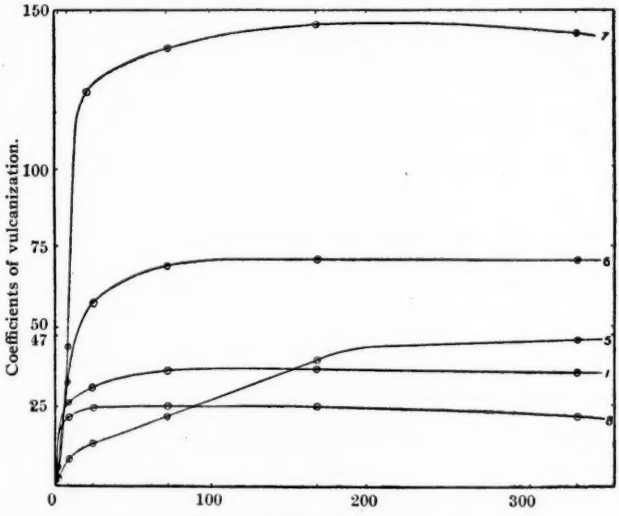


Figure 1

Small portions 1 in. by 3 in. were placed between glass microscope slides, pressed down, and tied into bundles. Vulcanization was carried out in an electrically heated oven with thermostat control. The center portions of the vulcanized sheets were taken for analysis. The material was cut or ground as finely as possible and extracted for six working days (about 48 hrs.) with acetone in a form of extractor in

[9] Stevens, *J. Soc. Chem. Ind.*, **38**, 195T (1919).

which the samples are surrounded by hot acetone vapor.[10] Those samples which were treated with hydrochloric acid-ether mixture were first extracted with acetone for four or five working days, then soaked in hydrochloric acid and ether for two or three days, and subsequently again extracted wth acetone. The extracted rubbers were oxidized and sulfur determined as barium sulfate in the usual manner.

The accompanying tables and graphs give the details of the results obtained. The calculation of the coefficient from the percentage of combined sulfur requires an allowance to be made for the mineral ingredients; both figures are, therefore, given in the tables.

Eight mixings were made of the following compositions:

No. of mix	1	2	3	4	5	6	7	8
Rubber	100	100	100	100	100	100	100	100
Sulfur	35	75	100	75	75	75	200	20
Zinc oxide	20	20	20	5	...	...	20	20
Zinc diethyldithiocarbamate	5	5	5	5	5	20	20	20

SERIES I—VULCANIZED AT 100°. ACETONE-EXTRACTED ONLY

% Combined Sulfur

Time of Vulcanization	No. of mix 4	5	6	7	8
2 hrs.	1.9	1.4	1.5	1.5	2.0
8 hrs.	16.4	4.8	16.6	12.9	13.7
24 hrs.	18.8	7.5	29.7	36.5	15.0
72 hrs.	22.6	11.9	35.1	40.6	15.6
168 hrs.	23.2	22.2	37.3	42.9	15.7
336 hrs.	22.6	25.6	37.3	42.0	13.7
		Coefficients			
2 hrs.	3.0	2.5	2.9	5.1	3.2
8 hrs.	26.2	8.6	32.4	43.9	21.9
24 hrs.	30.1	13.5	57.9	124.1	24.0
72 hrs.	36.2	21.4	68.5	138.0	25.0
168 hrs.	37.1	40.0	72.7	145.9	25.1
336 hrs.	36.2	46.1	72.7	142.8	21.9

The figures show that although there does not seem to be much difference in the rate of binding of the sulfur in the first hour or so, there are marked differences at the end of 8 hrs. All curves (Figure 1) are similar, including No. 6, which contains no zinc oxide, but a large proportion of zinc salt as accelerator. The curve given by No. 5 shows a more gradual slope owing to the slowness of combination with sulfur in the absence of zinc oxide and the presence of a relatively small amount of zinc salt, the total of combined sulfur in No. 5 after 336 hrs.' heating being 25.6% as against 37.3% for No. 6. The total of sulfur combined at the end of the experiments is greater the larger excess of sulfur present, and it would seem that there is no maximum limit to the coefficient given sufficient excess of sulfur and a sufficiency of accelerator.

The coefficients in the case of Nos. 6 and 7 are certainly greater than that required for the formula C_5H_8S, and this excess is not materially reduced if the whole of the zinc present be assumed to be converted into zinc sulfide and the sulfide sulfur reckoned as if combined with the rubber.

Another series of experiments limited to mixes 2 and 3 gave similar results. In this series the process for analysis of the products was extended to include extraction by a mixture of ether and hydrochloric acid which was preceded and followed by an acetone extraction as already described (p. 56).

[10] *Analyst*, **38**, 143 (1913).

In both cases coefficients are obtained much in excess of that required for the formula C_5H_9S in spite of the hydrochloric acid-ether treatment. This process was originally devised for soft rubber, and it is doubtful how far zinc sulfide if formed would have been removed by the treatment. No doubt the vulcanite would gradually absorb the acid solvent, but this might be a lengthy process. In connection with the hydrochloric acid treatment it is essential that the sample be immersed in the ethereal and not in the aqueous layer. If, therefore, an ordinary glass container be used for treating ebonite powders the quantity of concentrated hydrochloric acid added should not be more than just sufficient to separate from the ethereal layer.

SERIES II—VULCANIZED AT 100°. EXTRACTED WITH ACETONE AND WITH ETHER-HYDROCHLORIC ACID

Time of Vulcanization	% *Combined Sulfur* No. of mix 2	3
2 hrs.	2.4	2.2
8 hrs.	15.5	15.6
24 hrs.	22.4	21.3
72 hrs.	26.7	26.4
168 hrs.	29.7	30.8
336 hrs.	32.1	34.9
	Coefficients	
2 hrs.	4.8	5.0
8 hrs.	31.0	35.0
24 hrs.	44.8	47.9
72 hrs.	53.4	59.4
168 hrs.	59.4	69.3
336 hrs.	64.2	78.5

The two mixes in series II differ only in regard to percentage of sulfur. The curves (Figure 2) are similar in all respects, a larger proportion of sulfur resulting in a more rapid combination with sulfur and a higher final figure. If No. 3 be compared with No. 7 (Figure 1) the effect of a larger proportion of accelerator in effecting combination with sulfur is apparent.

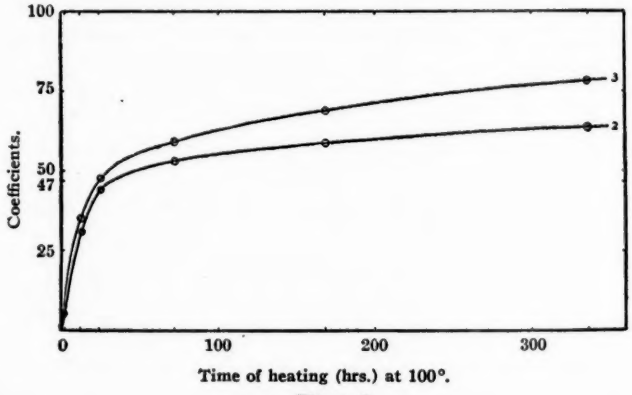


Figure 2

It will be remembered that graph 1 relates to specimens extracted with acetone only. Two specimens (Nos. 7 and 8 vulcanized for 168 hrs.) from this series were therefore extracted with hydrochloric acid-ether as well as with acetone in order to

provide a direct comparison. A large drop in values was obtained. The coefficient of No. 7 dropped from 145.9 to 73.5 and of No. 8 from 25.1 to 23.4. However, in spite of these reductions, the coefficient of No. 7 is still considerably in excess of that required for formula C_5H_8S.

The reduction cannot be explained on the assumption that it is brought about by decomposition of zinc sulfide formed from the zinc oxide and accelerator during vulcanization. The sulfide sulfur of Nos. 7 and 8 calculated in the form of coefficients would have been 7.9 and 1.4, respectively. This would have reduced the figures of 145.9 (for No. 7) to 136.6, still leaving a reduction in the coefficient of 63.1 to be accounted for.

The loss of combined sulfur appears to be to some extent dependent on the period of extraction with hydrochloric acid-ether mixture, as a repeat of the above-mentioned extraction of No. 7, but allowing the specimen to soak four weeks in the mixture, resulted in a figure for combined sulfur of 41.7%, corresponding to a coefficient of 72.5. This long extraction had removed most of the zinc, and the calculation of the coefficient was made after allowing for the 0.9% of ash retained.

Experiments were also made vulcanizing at a lower temperature (70°). The following figures were obtained:

SERIES III—VULCANIZED AT 70°. ALL SAMPLES EXTRACTED WITH ACETONE, ETHER-HYDROCHLORIC ACID, AND AGAIN WITH ACETONE

Time of Vulcanization	% *Combined Sulfur* No. of mix 2	3	4
8 hrs.	2.8	3.0	3.2
24 hrs.	6.2	6.4	6.2
72 hrs.	13.9	13.1	15.8
168 hrs.	19.1	18.9	20.2
336 hrs.	21.6	19.8	22.7
	Coefficients		
8 hrs.	5.6	6.9	5.7
24 hrs.	12.5	14.5	11.6
72 hrs.	27.8	29.6	29.3
168 hrs.	38.3	42.5	37.4
336 hrs.	43.4	44.7	42.0

The results as shown in Figure 3 indicate that combination with sulfur is much slower at 70° than at 100°. Toward the completion of the experiment combination is very slow indeed in spite of the presence of an ample excess of sulfur.

Vulcanization in Solution

A series of samples was vulcanized at 100° using a liquid mixture of *o*- and *p*-dichlorobenzene as solvent.

Four mixes were made as follow:

	A	B	C	D
Rubber	100	100	100	100
Sulfur	200	1000	1000	1000
Zinc oxide	20	20	....	....
Accelerator	20	20	20	40

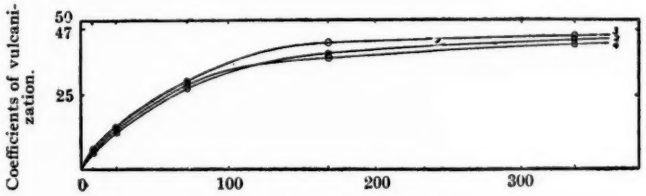
The accelerators used were: A and B, zinc diethyldithiocarbamate, C, tetraethylthiuramdisulfide, and D, the condensation product of pyridine and carbon disulfide, in conjunction with clay and zinc oxide. With the exception of C all had gelled after 1 or 2 hrs.' heating; C gelled later. The tubes were left in the oven for 168 hrs. All the tubes, particularly B, C, and D, gave off abundance of hydrogen sulfide. A portion from each tube was analyzed (as below). About 10 to 12 weeks

later the tubes were replaced in the oven for a further 242 hrs. at 100°, making a total of 410 hrs.

Analysis of the Samples Vulcanized for 168 Hours—The products were extracted for 40 hrs. with acetone, followed by 168 hrs.' soaking in ether-hydrochloric acid, and finally by 230 hrs.' extraction with acetone. Long acetone extractions are required to remove the dichlorobenzene as well as the free sulfur.

	A	B	C	D
Rubber (by diff.)	62.2	56.8	61.4	63.7
Sulfur	29.2	34.5	37.9	35.2
Ash	8.6	8.7	0.7	1.1
Corresponding coefficients	46.9	61.0	61.7	54.4

In the case of C and D the extracted product appeared to consist of two parts, a light yellowish powder and larger particles, almost black in color, but separate determinations of combined sulfur gave similar results.



Time of heating (hrs.) at 70°.

Figure 3

With the exception of A, which was prepared with the smallest proportion of sulfur, all coefficients exceed that required by the formula C_5H_8S, while A itself exactly corresponds to the formula. B and C, both prepared from mixtures containing the same excess of sulfur, gave approximately the same coefficient of 61. The coefficient given by C is particularly interesting as the mix was prepared without zinc oxide and by the help of an accelerator free from zinc. Any inaccuracy caused by the formation of zinc sulfide is therefore eliminated.

Analysis of the Samples Vulcanized for 410 Hrs.

	A	B	C	D
Rubber (by diff.)	59.1	52.0	64.3	65.0
Sulfur	32.3	39.3	35.0	33.9
Ash	8.6	8.7	0.7	1.1
Coefficients	54.7	75.6	54.5	52.2

The effect of continued vulcanization has been to bring out the influence of the zinc oxide and zinc accelerator which are present in compound B, which has now gone ahead of compounds C and D, which contain different accelerators. These latter show an actual decrease in coefficient similar to that observed with compounds 7 and 8, Series I.

The results show beyond all doubt that it is possible to prepare vulcanizates containing an appreciably greater percentage of combined sulfur than that required by the formula C_5H_8S.

Having regard to the considerable amount of hydrogen sulfide evolved in the formation of the vulcanizates, it is possible that part of the combined sulfur results from the substitution of sulfur for hydrogen in the rubber molecule.

These vulcanizates are probably much overvulcanized in the technical sense; consequently, it is probable that only small quantities of these substituted products

are contained in a normally made vulcanite. To produce a higher coefficient than 47 necessitates the use of a very large excess of sulfur.

The Vulcanization of Rubbers Containing Varying Amounts of Protein

Three specimens of raw rubber were used: (1) latex sprayed "whole rubber" containing approximately 10% of additional serum constituents; (2) ordinary crepe rubber as control; (3) a protein-poor rubber prepared by coagulating latex purified by centrifuging twice[11] and giving the following analytical figures: nitrogen 0.13%, "resins" 2.1%, ash 0.10%.[12] Vulcanite mixes were made up according to formula 2 and vulcanized in the electric oven for 480 hrs. at 70°. The vulcanizates were extracted with acetone, hydrochloric acid-ether, and again with acetone as before.

The following figures were obtained:

	% Combined Sulfur	
1	2	3
16.90	17.55	18.75
	Coefficients	
33.8	35.1	37.5

If the coefficient for (1) is corrected by making allowance for 10% of non-rubber ingredients retained from the serum we obtain the figure of 37.2, and similarly the crepe control will contain ingredients not present in the purified sample, which will have the result of raising the coefficient. Consequently, it appears that all three specimens give substantially the same coefficient if this be calculated on the rubber hydrocarbon. The non-rubber constituents have therefore had no effect on the total amount of sulfur combined.

Progressive Extraction of Vulcanites with Acetone

Two mixes were made up as follows:—

	X	Y
Rubber	100	100
Sulfur	75	75
Zinc oxide	20	20
Zinc sulfide	...	5
Zinc diethyldithiocarbamate	5	...

Mix X was vulcanized for 336 hrs. at 100° in the manner previously described, and Y was press-cured for 4½ hrs. at 55 lb. steam pressure (150°). About two grams of each were extracted with acetone, and determinations of the sulfur in the extract made at varying periods.

The following results were obtained:

PER CENT FREE SULFUR EXTRACTED

Time Extracted, (Hrs.)	X		Y	
	Total	Increase	Total	Increase
44	7.50	..	9.50	..
88	7.98	0.48	9.92	0.42
176	8.39	0.41	10.34	0.42
264	8.54	0.15	10.57	0.23
440	8.75	0.21	10.81	0.24
660	9.03	0.28	11.95	1.14
836	9.18	0.15	12.09	0.14
1012	9.27	0.09	12.15	0.06
1210	9.41	0.14	12.23	0.08

[11] Kindly supplied by de Vries.

[12] *Arch. Rubbercultuur*, **12**, 562 (1928).

These figures are illustrated in Figure 4. In view of the exceptional rise in quantity of sulfur extracted in the case of the compound Y at the end of 660 hrs., i. e., 5th fraction, it may be stated that a duplicate series of extractions, carried out in "parallel" with those for which figures are here given, gave a similar result, the increment being 1.15% of sulfur at the end of about 500 hrs.' extraction, and occurring again in the case of Y only.

When the bulk of the acetone is distilled off from any fraction there is left a brown liquid, and in the case of the first fraction there is the usual deposit of sulfur crystals. The brown liquors from several fractions were filtered from sulfur and united, and after oxidation yielded 0.28% of sulfur for X and 0.26% for Y, which

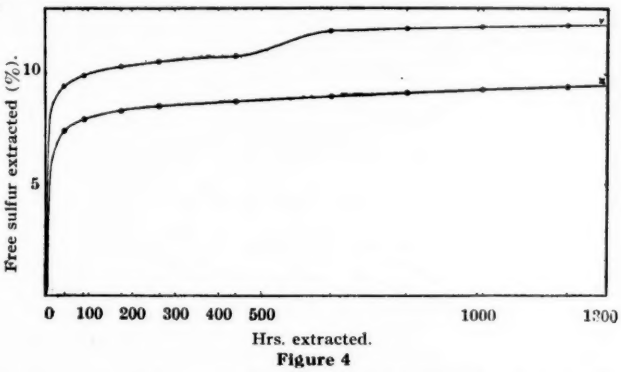


Figure 4

amounts are approximately equivalent to the solubility of sulfur in acetone under the conditions of the experiments. The sulfur in the brown extract of both X and Y is therefore fully accounted for by sulfur normally soluble in acetone, and the brown color does not therefore indicate decomposition products of vulcanites containing sulfur. The figures for the sulfur extracted indicate that although the bulk is removed in a week (40 hrs.) small quantities continue to be extracted for an indefinite period. After 264 hrs. there is no tendency for the amount of sulfur, extracted in a given period, to fall—in fact, in the case of the "high temperature" vulcanite it tends rather to increase; except for this the behavior to acetone of "low temperature" and "high temperature" vulcanites is the same.

Conclusions

(1) At low temperatures by means of accelerators it is possible to produce vulcanites containing "combined sulfur" considerably in excess of that required for the formula C_5H_8S. Such vulcanites may be obtained by vulcanizing at 100° with a variety of ultra-accelerators with and without zinc oxide as an activator. If zinc oxide or a zinc salt is used the excess coefficient cannot be explained by the presence of the zinc sulfide in the vulcanite.

(2) The amount of sulfur combined with the rubber, given sufficient heating and presence of accelerator, is mainly dependent on the excess of sulfur present.

(3) Extraction of the vulcanite with hydrochloric acid-ether mixture removes a part of the "combined" sulfur. A considerable amount is removed when the amount of combined sulfur is very large, but even then the amount of sulfur remaining is considerably in excess of that required by the formula C_5H_8S.

(4) Vulcanization at low temperatures in solution in accordance with Whitby's procedure with the aid of accelerators also yields vulcanites with coefficients in excess of that required for the formula C_5H_8S.

(5) The result of vulcanization at low temperatures is approximately the same, whether the rubber contains all the protein and serum ingredients, the usual proportion, or very little.

(6) Extraction of sulfur from vulcanite with hot acetone vapor is not complete after 1210 hrs.

(7) Having regard to the hydrogen sulfide and other volatile sulfur compounds evolved in appreciable quantities during vulcanization, it is evident that part of the combined sulfur results from substitution of hydrogen by sulfur. This substituted product is decomposed by the hydrochloric acid-ether mixture. It may not be possible to decompose the whole in this manner. Consequently, any "combined" sulfur in excess of that required by the formula C_5H_8S may result from substitution in the molecule.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 6, page 553. June, 1929.]

Some Observations on Rubbers with Low Nitrogen Content[1]

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Rubber has been prepared protein-free, although not entirely nitrogen-free, by digesting latex with caustic soda, as recommended by Pummerer and Pahl. Rubbers with a nitrogen content of from 0.004–0.009% per cent have been prepared by a slight modification of the original procedure. This rubber can be compounded and cured to give good quality vulcanizates, which compare very favorably with the controls. Protein-free rubber, when acetone-extracted, becomes nitrogen-free. This can still be vulcanized, although it cures slowly. The rate of cure of rubber from protein-free latex is affected very little by the pH of the coagulating medium whereas with full-nitrogen rubber rate of cure varies considerably with change in pH value at the time of coagulation. It was also found that protein-free rubber could be racked. Data on the preparation, coagulation and nitrogen content as well as the vulcanization results of protein-free rubber are presented. The observations lead to the conclusion that protein is not the key to the explanation of the physical properties of rubber.

SINCE it was first discovered that rubber contained protein, many researches have been carried out to determine just what part this material played in the structure and properties of the rubber. The present work shows that the protein is of less importance than has often been supposed.

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

Note—Some confusion exists regarding the terms "protein-free" and "nitrogen-free." Most of the published articles fail to mention what method was used for proving the absence of nitrogen. Consequently it is often difficult to tell whether the terms may be synonymous. In this paper "nitrogen-free" will be used only with reference to rubber containing an amount of nitrogen which cannot be detected by sensitive colorimetric methods. Rubber containing a known amount or an unstated percentage above 0.001 per cent will be called "nitrogen-poor" or "protein-free."

Many attempts have been made in this laboratory to prepare pure rubber hydrocarbon free from nitrogen or protein and to test its physical properties when vulcanized. This seemed more important than ever in view of the work reported by Dinsmore[2] in which it was found that rubber coagulated from latex under varying pH values showed widely different rates of cure and physical properties. The effects noted were attributed to different conditions of the rubber protein as determined by the pH value of the latex at the time of coagulation. However, more definite proof seemed desirable and it was decided to repeat in part the work mentioned above using protein-free latex prepared according to the method of Pummerer and Pahl.[3] Previous investigators have stated, as noted below, that they have prepared nitrogen-free rubber, but there are few, if any, data available in the literature as to the exact procedure used in determining the absence of nitrogen or of protein, or as to the physical properties of the vulcanizates formed from such rubbers. For these reasons it was decided to carry out the present research.

Historical

Beadle and Stevens[4] have investigated the influence of the insoluble constituent on the physical properties of vulcanized rubber. They prepared from smoked sheet a sample of rubber poor in nitrogen and another rich in nitrogen. The nitrogen-poor rubber combined with sulfur very slowly and gave a poor vulcanizate, while the nitrogen-rich sample vulcanized more rapidly than the control and gave better physical properties.

Spence and Young[5] have also shown that the lower the quantity of nitrogen in the rubber the more slowly sulfur entered into combination.

Stevens[6] has investigated the influence of additions of various substances on the vulcanization of smoked sheet from which most of the insoluble matter had been removed. The results confirm previous conclusions regarding the importance of the insoluble matter. Peptone, casein, and litharge all speeded up the cure. The effect of the absence of the insoluble matter is essentially to reduce the rate of vulcanization. A sample cured for a very long time showed results approximating those given by the original, untreated rubber.

[2] Dinsmore, IND. ENG. CHEM., **18**, 1140 (1926).
[3] Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).
[4] Beadle and Stevens, *India Rubber J.*, **44**, 554, 603 (1912).
[5] Spence and Young, *Kolloid-Z.*, **13**, 265 (1913).
[6] Stevens, *Ibid.*, **14**, 91 (1914).

Eaton and Grantham[7] found that the addition of casein or peptone had little effect on the rate of cure in rubber already containing the insoluble matter.

Freundlich and Hauser[8] digested latex with trypsin and found that on coagulation by the usual methods the rubber came down in a lump, apparently without first forming a flocculent precipitate.

Feuchter[9] compared the tensile properties of KD rubber (ether-soluble diffusion rubber, protein-free) with those of smoked sheet cured equal periods of time in a mix containing rubber, zinc oxide, accelerator, and sulfur. There was practically no difference in the two rubbers as shown by tensile at break and at 500 per cent elongation.

More recently Pummerer and Pahl[3] purified rubber by treating latex with caustic soda until free from protein and state that its capacity for vulcanization was normal.

Hauser has reported that the soluble and insoluble fractions from protein-free rubber when combined vulcanize approximately equal to the original. Later, however, Pummerer, Andriessen, and Gündel[10] state that the "total rubber" made by the caustic process from ammonia-preserved latex,

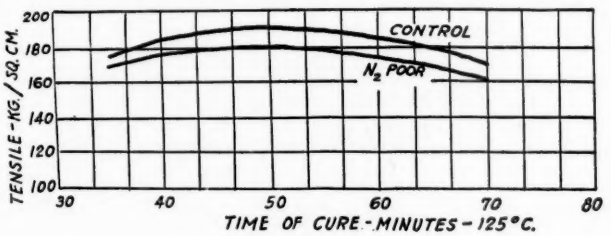


Figure 1—Preliminary Test

although fairly protein-free, was not nitrogen-free, and conclude from an analysis that the residual nitrogen is present as amine nitrogen and not as protein nitrogen.

Protein in rubber has often been connected with the mechanism of coagulation of latex and the physical structure of the resulting coagulum. The changing opinion of rubber technologists in regard to the importance of the protein as an aid in explaining rubber behavior is reflected in a statement by De Vries[11] that "it seems probable that the protein will have to be more or less dethroned and driven back to the second plane as our knowledge advances." An investigation by the same author[12] on rubber containing 0.03 per cent or less of nitrogen indicated that the "absence of proteins had not caused striking changes in the coagulation phenomena."

[7] Eaton and Grantham, *J. Soc. Chem. Ind.*, **35**, 715 (1916).

[8] Freundlich and Hauser, *Kolloid-Z.*, Spec. No., April 1, 1925, p. 15; *India Rubber J.*, **69**, 663, 693 (1925).

[9] Feuchter, *Gummi-Zig.*, **40**, 1691 (1926).

[10] Pummerer, Andriessen, and Gündel, *Ber.*, **61**, 1583 (1928).

[11] De Vries, *Trans. Inst. Rubber Ind.*, **3**, 284 (1927).

[12] De Vries, *Caoutchouc & gutta-percha*, **23**, 13,082 (1926).

Experimental

In this investigation 30 per cent ammonia-preserved latex from the Goodyear plantations was used. It was treated with 2 per cent sodium hydroxide solution according to the method of Pummerer and Pahl.[3] The resulting cream was washed, dialyzed, coagulated with acid, and a sample dried *in vacuo*.

A Kjeldahl determination was made using Nessler's method

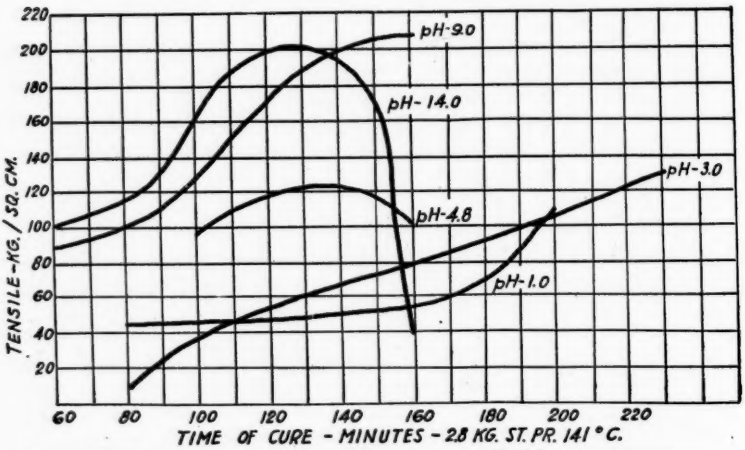


Figure 2—Maximum Tensile, Rubber-Sulfur Mix. Full Nitrogen Content. Data from Dinsmore[2]

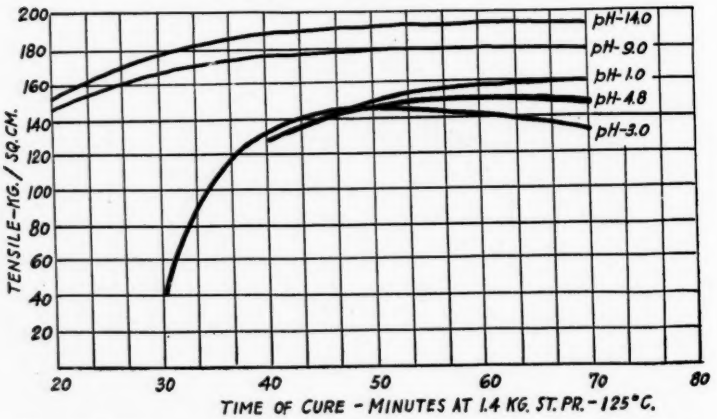


Figure 3—Maximum Tensile, Mercapto Stocks. Full Nitrogen Content. Data from Dinsmore[2]

for estimation of the ammonia produced. The result showed about 0.015 per cent nitrogen. The major portion of the coagulum was air-dried after addition of a synthetic antioxidant. On vulcanization this showed tensile properties substantially equal to rubber from latex which had received just heat treatment for the same length of time as the alkali-purified latex (Figure 1).

As an attempt to produce a more nearly nitrogen-free product than this first lot, a run was made doubling the changes of caustic. After the sixth change of alkali the caustic layer separated water-white, and on test with permanganate in very dilute solution the green manganate stage was still present at the end of 24 hours. Analysis of the cream after washing showed 0.004 per cent nitrogen calculated on the dry rubber.

As it seemed to be of considerable interest to find out the effect of pH of the coagulating medium on the properties of

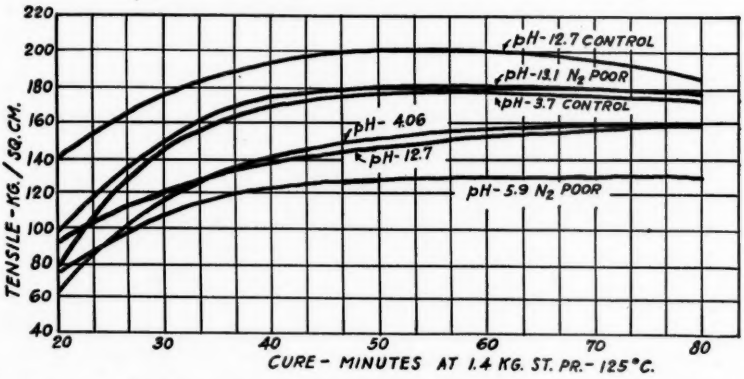


Figure 4—Maximum Tensile, Accelerated Stocks. Nitrogen-Poor Rubbers

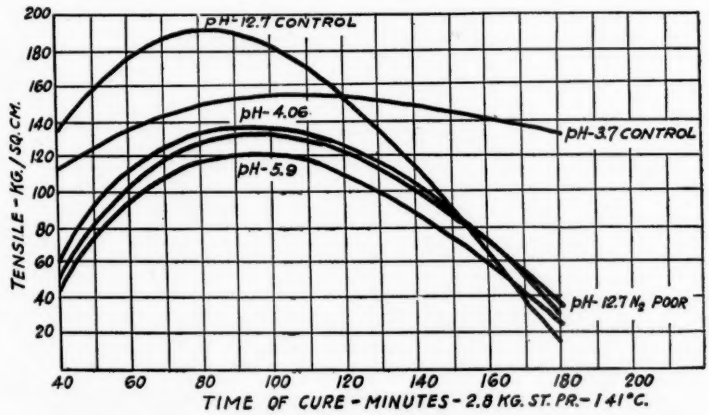


Figure 5—Maximum Tensile, Rubber + Sulfur. Nitrogen-Poor Rubbers

this protein-free rubber, rather large quantities of the purified latex were prepared, the caustic being changed six times in every case. The nitrogen content ran from 0.006 to 0.009 per cent.

Coagulation was carried out by addition of the treated latex to excess of alcohol to which had been added suitable amounts of acid or alkali. The pH of the serum was determined by means of the hydrogen electrode. The coagulum

was then washed and, as it oxidized very rapidly, was treated with 5 per cent of a commercial antioxidant before drying.

As suggested in the most recent article by Pummerer,[10] a specimen of the protein-free rubber analyzing 0.009 per cent nitrogen was extracted with acetone. This reduced the nitrogen content to so low a value that it could not be accurately measured by the method used. This rubber was vulcanized in the same type formulas as the other rubbers, but without antioxidant.

It is also worthy of note that the rubber with low nitrogen content could not be plated out readily by electrolysis. The absence of the protein renders the rubber too good an in-

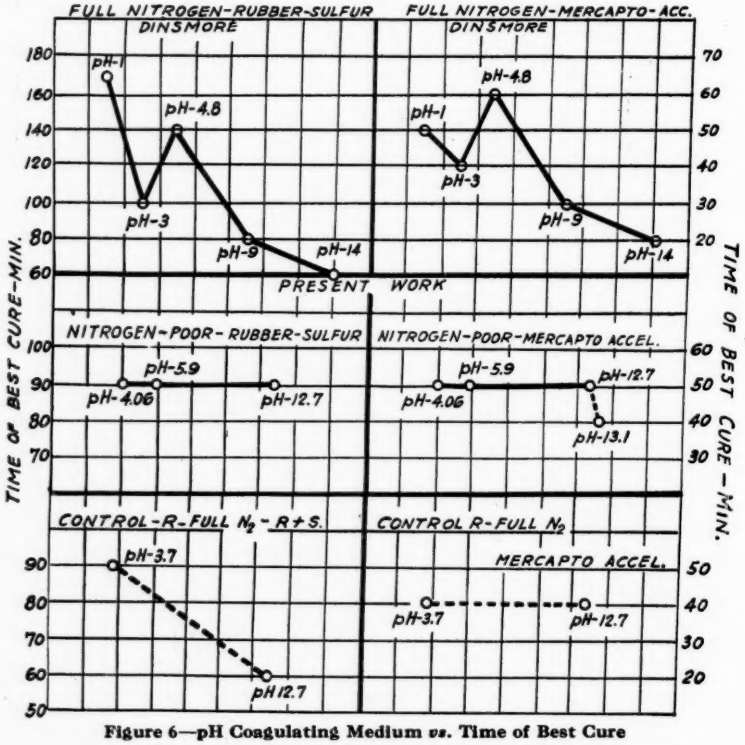


Figure 6—pH Coagulating Medium *vs.* Time of Best Cure

sulator, so that even a thin film had great resistance. The addition of a solution of sodium chloride gave increased conductivity and permitted the building up of a film of nitrogen-poor rubber by electrolysis. The nitrogen-poor rubber could also be racked.

Controls were prepared as follows:

(1) Latex was heated for the same length of time and at the same temperature as the lots from which the protein was removed. This was coagulated at pH 12.7. It was, of course, impossible to duplicate the effect, if any, of the caustic on the rubber hydrocarbon.

(2) Latex which had received no special treatment at all was coagulated at pH 3.7.

The rubbers prepared as described above were compounded in two formulas as follows:

	Rubber-Sulfur Mix	Accelerated Mix
Rubber	100.00	100.00
Zinc oxide	5.00	5.00
Sulfur	10.00	3.00
Stearic acid	1.50	1.50
Antioxidant	5.00	5.00
Captax	...	0.50

Both mixes were cured in a steam platen press, the accelerated mix at 125.6° C. (258° F.) and the rubber-sulfur mix at 141.7° C. (287° F.). The physical tests were made on an autographic stress-strain machine. The best cures were determined by hand tests.

Discussion of Results

The complete curing data are shown in Table I. The results are plotted graphically on Figures 2 to 5. Figures 2 and 3, showing the results described by Dinsmore,[2] are given as a matter of reference. On Figure 6 the times of best cure are plotted and compared with the results obtained in previous work. It should be noted that the rate of cure of the nitrogen-poor rubbers is quite constant in both formulas, while in the full-nitrogen rubbers it varies according to the pH value existing at the time of coagulation. This difference is more noticeable in the pure-gum mix than in the accelerated stock.

The physical properties of the nitrogen-poor rubber (Figure 5) are also more uniform in the pure-gum mix than is the case with rubbers having full protein content (Figure 2). Results at different pH values are in close agreement. Good vulcanizates are obtained. The difference from the controls is relatively small and is probably due to the activating effect of hydrogen ions on the protein in the controls. There is not so much difference between the accelerated stocks containing little nitrogen (Figure 4) and the same type of stocks as reported by Dinsmore (Figure 3).

The acetone-extracted sample of nitrogen-poor rubber (Table I) showed somewhat lower physical properties in both types of test formulas. No acetone-extracted control was tested. The data at hand do not warrant a statement as to whether the low physical properties are due to the total absence of original nitrogen, or whether the results on the unextracted samples were benefited by the addition of the nitrogenous antioxidant or by the presence of other acetone-soluble constituents.

However, the antioxidant added to this protein-free rubber does not affect the rate of cure or physical properties of a rubber mix using standard plantation rubber. It is more probable that the effect in the unextracted samples is due to the small amount of nitrogenous constituent remaining in the rubber. This residual nitrogen may be that mentioned

by Midgley in recent papers before the AMERICAN CHEMICAL SOCIETY as having a marked effect on the physical properties of rubber. Further tests are to be made on this subject.

Table I—Curing Data

RUBBER	pH	CURE		TENSILE			ELONGATION AT BREAK
		Time	State hand test	400%	600%	Break	
		Min.		*Kg. per sq. cm.*			%
UNACCELERATED STOCKS—CURED AT 2.8 KG. PER SQ. CM. AND 141.7° C.							
Protein-free	4.06	40	U.	13	25	60	795
		60	U. G.−	14	28	116	860
		90	B.	17	36	129	795
		120	G.+S.O.	21	50	133	745
		180	B. O.	26	..	30	440
	5.9	40	U.	11	20	44	825
		60	U.	12	23	76	850
		90	B. G.+	17	39	120	780
		120	O.	22	53	113	710
		180	B. O.	..	..	24	350
	12.7	40	U.	10	19	50	850
		60	U. G.−	13	26	89	850
		90	B. G.+	18	37	134	800
		120	O.	19	43	125	750
		180	B. O.	27	..	36	465
Controls: Not heated	3.7	40	U.	14	33	114	845
		60	G.−	17	40	133	810
		90	G.+	19	47	152	795
		120	O.	23	62	138	720
		180	B. O.	29	83	133	675
Heated	12.7	40	U.	14	31	134	855
		60	G.− B.	18	44	177	820
		90	G.+	25	68	190	750
		120	B. O.	31	108	126	590
		180	B. O.	..	..	18	225
ACCELERATED STOCKS—CURED AT 1.4 KG. PER SQ. CM. AND 125.6° C.							
Protein-free	4.06	20	U.	10	19	64	850
		30	U.	14	29	116	830
		40	G.−	15	33	124	800
		50	B.	17	37	138	790
		80	O.	20	51	160	755
	5.9	20	U.	11	20	74	850
		30	U.	13	26	109	865
		40	G.−	13	28	104	825
		50	B.	16	36	126	800
		80	O.	18	44	130	755
	12.7	20	U.	11	20	93	890
		30	U.	13	23	100	850
		40	G.−	15	31	120	815
		50	B.	17	34	145	830
		80	O.	20	49	160	775
	13.1	20	U.	12	25	96	850
		30	G.−	15	33	124	820
		40	B.	19	49	176	800
		50	G.+	22	64	160	735
		80	O.	26	89	179	715
Controls: Not heated	3.7	20	U.	11	23	77	825
		30	G.−	17	40	145	815
		40	B.	19	48	168	805
		50	G.+	21	58	178	780
		80	O.	23	68	176	755
Heated	12.7	20	U.	15	34	140	830
		30	G.−	17	38	172	835
		40	B.	19	47	193	805
		50	G.+	21	55	190	780
		80	O.	22	63	184	755

Table I—Curing Data *(Continued)*

Rubber	pH	Cure		Tensile			Elongation at Break
		Time	State hand test	400%	600%	Break	
		Min.		*Kg. per sq. cm.*			%
NITROGEN-POOR—ACETONE-EXTRACTED—NO ANTIOXIDANT—UNACCELERATED —CURED AT 2.8 KG. PER SQ. CM.							
		60	U.	5	8	25	895
		80	U.	7	11	44	895
		120	G.−	10	19	104	880
		160	B.	15	29	127	805
		240	B. O.	..	..	15	265
ACCELERATED—CURED AT 1.4 KG. PER SQ. CM.							
		20	U.	5	8	45	955
		30	U.	7	13	91	920
		40	G.−	9	16	107	910
		50	G.−	9	19	116	885
		80	B. G.+	13	28	131	820

U = Under. G. = Good. B. = Best. S. O. = Slightly over. B. O. = Badly over.

The rate of cure as measured by the combined sulfur determined on the best cures is given in Table II. The small amount of nitrogen present in the samples does not seem to have retarded the combination of sulfur. This is not in agreement with the findings of earlier investigators, but here again it is possible, although not probable, that the nitrogenous antioxidant may have influenced the results.

Table II—Rate of Cure as Measured by Combined Sulfur on Best Cures

Rubber	pH	Nitrogen Content	Unaccelerated		Mercapto	
			Best cure	Combineb sulfur	Best cure	Comdined sulfur
		%	*Min./kg./ sq. cm.*	%	*Min./kg./ sq. cm.*	%
Protein-free	4.06	0.0085	90/2.8	2.26	50/1.4	1.76
	5.9	0.0096	90/2.8	2.06	50/1.4	1.76
	12.7	0.009+	90/2.8	2.26	50/1.4	1.68
	13.1	0.006	....	..	40/1.4	1.80
Full nitrogen	3.7		90/2.8	2.15	40/1.4	1.38
	12.7		60/2.8	1.85	40/1.4	1.64

Conclusions

Rubber cannot be prepared absolutely nitrogen-free by the method of Pummerer and Pahl, even though the treatment of the latex with caustic is continued twice as long as they recommend. The residual 0.004 to 0.009 per cent of nitrogen is not protein nitrogen, since it is removable by acetone extraction and the amount of nitrogen falls so low as to be unmeasurable with accuracy by the exact method used in this research—i. e., colorimetric determination with Nessler's solution. The authors note with satisfaction that Pummerer has come to exactly the same conclusion.

Comparison of the results of vulcanizing protein-free rubber with those of the controls and with the results of the

previous research shows that the rate of cure is constant under different conditions of coagulation and that the quality of the nitrogen-poor vulcanizates compares very well with the controls and with the earlier mentioned work described by Dinsmore.

It appears, therefore, that the variation in cure and quality as noted by Dinsmore was due entirely to some particular condition of the rubber protein brought about by the varying pH values existing at the time of coagulation.

Protein-free rubber, after acetone extraction, is practically nitrogen-free and cures slowly to give vulcanizates of lower quality than is obtained with the protein-free rubber. It should be remembered, however, that, as stated above, this effect may not be due entirely to the absence of nitrogen. Definite conclusions on this phase of the question must be withheld until more experiments are made.

The evidence presented shows that protein-free rubber can be compounded and cured to give good quality products. Hence the protein is not an essential factor in producing the physical properties of vulcanized rubber. The condition of the protein does affect the rate of cure and so exerts an indirect effect upon the quality of the rubber.

Acknowledgment

The writers' thanks are due R. P. Dinsmore, chief chemist of the Goodyear Tire & Rubber Company, for permission to publish this paper.

[Reprinted from the Journal of the American Chemical Society, Vol. 51, No. 4, page 1216. April, 1929.]

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. I. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF NATURAL RUBBER

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED NOVEMBER 2, 1928 PUBLISHED APRIL 5, 1929

The destructive distillation of rubber has been studied by many investigators. Isoprene and dipentene have been isolated many times, identified and shown to be the predominating products. The existence of other products has often been detected and empirical names have been given to them. Ipatiew and Wittorf[1] have positively identified trimethylethylene; Harries[2] identified myrcene and also a terpene with a boiling point of 168–169°. Heveen (b. p. 252°) was found by Bouchardat[3] and Staudinger[4] recently has isolated two compounds which he believes to be dimethylbutadiene and tetrahydrotoluene. Staudinger and associates[4,5] also state that in the distillate from destructive distillation at reduced pressure only isoprene and dipentene are present in the fraction below 200°.

The present work was undertaken largely for the purpose of throwing light upon the structural formula of the rubber hydrocarbon and, although this objective has not been attained, it is hoped that an extension of the methods of prediction developed herein to the constitution of heveen, $C_{15}H_{24}$, may eventually yield constructive results.

Procedure

Two hundred pounds of light pale crepe were destructively distilled at atmospheric pressure, in 16-lb. batches in an iron vessel connected to a suitable condensing system. No attention was paid to temperature control, due to the large size of the batches; the temperature was always raised as quickly as possible to about 700°, in order to obtain a favorable yield of isoprene, which was desired for work on synthetic rubber. The distillate is a dark-colored oil. After removal of isoprene by fractionation, the residual oil was subjected to thorough fractional distillation in a carborundum-coated spiral column.[6] Cuts were made for every degree between 50° and 176°. The customary volume of an intermediate was 5 cc., except where components were detected within 4° of each other,

[1] Ipatiew and Wittorf, *J. prakt. Chem.*, **55**, 2 (1897).
[2] Harries, *Ber.*, **35**, 3662 (1902).
[3] Bouchardat, *Bull. soc. chim.*, **24**, 108 (1875).
[4] Staudinger, *Helv. Chim. Acta*, **9**, 549 (1926).
[5] Staudinger, *ibid.*, **9**, 529 (1926).
[6] T. Midgley, *Ind. Eng. Chem.*, **20**, April (1929).

in which case the intermediates were larger. Several components were present to the extent of 50 cc. or more, and in such cases accurate and positive identification could be made. In other instances, 10 or 15 cc. was the maximum amount to work with. Such cases are recorded in the data only when the identification was sufficient to be certain of the series to which the component belonged.

It was later discovered that the addition of magnesium to the rubber greatly increased the yield of materials other than isoprene and dipentene. Zinc, iron, and aluminum have a similar effect but to a very much smaller extent; copper is without effect; brass equals iron. A batch of 16 lb. of rubber was destructively distilled in the presence of 850 g. of magnesium and the product separately investigated. The same components were found that had been identified in the distillation of rubber alone but the proportions were different. The material from the distillation with magnesium is richer in compounds of the aromatic series and poorer in chain compounds. The liberty has been taken only in the cases of a few of the chain compounds, which were present in both cases in extremely small quantity, of combining the same cuts in order to obtain a sufficient sample to work with.

Wherever two or more components could not be separated to purity by fractional distillation, other methods of purification were used. Distillation from aniline proved to be very useful in separating chain from hydro-aromatic compounds. Compounds of the aromatic series were treated with bromine to eliminate the ethylenic impurities and steam distilled.

Cuts were considered suitable for identification: (1) when the Engler distilling range was less than 2°, (2) when special tests gave positive identification of the presence of a compound in the bulk, (3) when the compounds present could each be identified separately and the physical properties of the mixture checked this analysis (this has been done in only one case when more than two compounds were present) or (4) when continued purification failed to alter the physical properties.

In general, physical constants were relied upon for identification. These were augmented by titration of the unsaturation with a KBr–$KBrO_3$ mixture and by determination of the molecular weight. Quantitative hydrogenation with platinum black, followed by removal of the aromatic compounds by nitration, played an important part in many identifications. Special tests were used when found in the literature. Combustion was used in cases where the C–H ratio was in doubt.

Due to the small quantity of hydrocarbon left after other methods of identification had been exhausted, the location of double bonds with potassium permanganate was rendered impracticable. Consequently, where the comparison of physical constants is not sufficiently accurate to locate a double bond or where the constants are lacking in the literature,

the exact position of the double bond remains in doubt. The location is actually being determined by ozonation and will be reported later.

In addition to the components which could be separated by fractional distillation, a substantial proportion of the original material polymerized, remaining as a jelly in the distilling flask. It may be safely assumed that the materials lost in this way consisted very largely of dienes which were too unstable to distil.

Results

Briefly stated, the materials found were olefinic, dienic, aromatic and hydro-aromatic compounds, and a single dicyclic olefin. No fully saturated compound was detected. Table I lists the names of the compounds, the degree of accuracy of their identification and the relative quantities present in the two types of distillates.

The following paragraphs describe more completely each compound listed in the table. The common or Geneva name is used to initiate the paragraph when positive identification has been secured. It is followed by the physical constants from "International Critical Tables" (abbreviated as I. C. T.) or other sources, which are then indicated. The next listed item is the method of purification, followed by the physical constants of the purified substance. Additional data include special tests, constants of the hydrogenated compounds, special observations, etc. Where no positive identification is possible, the paragraph is headed by the word COMPONENT, followed by the physical constants found and any other data bearing on the partial identification. The boiling point ranges refer to Engler distillation from the ten-to-ninety-per cent over points and unless otherwise stated densities are at 20°/20° and indexes of refraction at 20°.

3-Methyl-1-Butene.—B. p., 21°; d, 0.660; n not given; mol. wt., 70. Purified by fractional distillation: b. p., 19–20°; d_{20}^{15}, 0.645; n^{18}, 1.3897; mol. wt., 66.8; double bond, 1.35. Although the material obtained was impure, there can be no doubt that the major part of it was 3-methyl-1-butene. It probably contained a low-boiling diene as impurity.

2-Methyl-1-Butene.—B. p., 32°; d_0^0, 0.667; n^{17}, 1.378. Purified by polymerization of the contained isoprene with sodium–potassium alloy, removal of the polymerized product, reduction of the remaining isoprene by sodium in liquid ammonia and subsequent fractional distillation: b. p. 30–31°; d_{20}^{17}, 0.6645; n^{17}, 1.3752; double bond, 1.0.

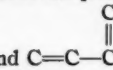
Isoprene.—B. p., 34°; d, 0.679; n, 1.4221. Purified by fractional distillation, identified by polymerization to synthetic rubber: b. p., 33–34°; d, 0.671; n, 1.4103. Bromination indicates 1.82 double bonds per C_5H_8. Pentenes were present as impurities.

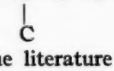
2-Methyl-2-Butene.—B. p., 38.4°; d^{13}, 0.668. Purified by fractional distillation: b. p., 36.8–38°; d, 0.666; n, 1.3927; double bonds, 1.25 per C_5H_{10}. Isoprene present as impurity.

Component 59–60°.—d, 0.730; n, 1.4117; 1.0 double bond per C_6H_{12}. Purified by fractional distillation. Hydrogenation and nitration gave a material, b. p., 60–61°; d, 0.654; n, 1.3728; mol. wt., 87. I. C. T. gives for 2-methylpentane: b. p., 60°; d, 0.654; n, 1.372; mol. wt., 86. These results identify the original material as a 2-methylpentene, position of the double bond unknown.

3-Methyl-2-pentene.—Isomer No. 1: b. p., 65.7°; d^{15}, 0.722; *n*, 1.4065. Isomer No. 2: b. p., 70.2°; *d*, 0.698; *n*, 1.401. Purified by fractional distillation: b. p., 62–65°; *d*, 0.694; *n*, 1.404; double bond, 1.07 per C_6H_{12}. Hydrogenation gave a compound b. p., 63.6–64.5°; *d*, 0.666; *n*, 1.3752; mol. wt., 86. I. C. T. gives for 3-methylpentane: b. p., 64°; *d*, 0.668, *n*, 1.377, mol. wt., 86.

Component 76–79°.—Purified by aniline fractionation: *d*, 0.742; *n*, 1.4346; double bonds, 1.58 per C_6H_{10}. Partially hydrogenated, then extracted with H_2SO_4; adding water to the acid liberates an oil which gave on redistillation: b. p. 67–68°; *d*, 0.712; *n*, 1.4060; mol. wt., 83. Bromine reacted slowly. I. C. T. gives for 3-methyl-2-pentene two isomeric forms of which the average is: b. p., 67.8°; *d*, 0.712; *n*, 1.4039; mol. wt., 84. The following deductions may be made: 1.58 double bonds shows the presence of a diene in the original material; the partial hydrogenation and the extraction show that the carbon structure of this diene corresponds to 3-methyl-pentadiene. The forms compatible with the experimental results are: C=C—C=C—C, C=C=C—C—C

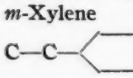
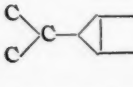
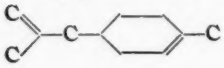




and C=C—C—C—C. The only diene given in the literature boiling at 76–79° is 3-methyl-1,3-pentadiene, for which the constants by Abelmann are: b. p., 76–79°; d_4^0, 0.7576, $n^{16.5}$, 1.45427. A mixture of 64% of this diene, 31% of 3-methyl-2-pentene

TABLE I

COMPOUNDS, IDENTIFICATION, AND QUANTITIES

Compounds	Degree of identification	% in distillate Straight	% in distillate With Mg
C—C(C)—C=C	Positive	0.04	0.2
C=C(C)—C—C	Positive	.04	.2
C=C(C)—C=C	Positive	10.0	10.0
C—C(C)=C—C	Positive	.04	.2
C—C(C)=C—C—C Δ?	Chain structure positive	.06	.30
C—C—C(C)=C—C	Positive	.03	.15
C=C—C(C)=C—C	Positive except for position of double bonds	.03	.15
Benzene	Positive	.005	.1
C—C—C(C)=C—C—C	Chain structure positive	.03	.15
Δ^3—C—C_6H_9	Not positive	.01	.1
Δ^2—C—C_6H_9	Suspected	..	..
C—C=C—C—C—C(C)—C Δ?	Chain structure positive	.02	.1
Δ^1—C—C_6H_9	Positive	.1	1.0
Toluene	Positive	.05	1.0
C—C—C—C—C—C(C)=C Δ?	Chain structure positive	.04	.2
Dihydro-*m*-xylene	Positive	.1	1.0
m-Xylene	Positive	.05	1.0
	Positive	.08	.8
	Hydrogenation product		
p-Methylethylbenzene	Positive	.04	.8
$C_{10}H_{18}$ (1 double bond)	.....	.04	.8
C—C(C)=C—C—C—C(C)=C—C Δ?	Not positive	.015	0.0
	Positive	20.0	20.0

and 5% benzene will yield physical constants in close agreement with those of the original mixture. 3-Methyl-2-pentene and benzene are the adjoining and identified components. The identification is not considered as positive, despite the strong evidence.

Benzene.—M. p., 5.6°; b. p., 79.6°; *d*, 0.878; *n*, 1.5014.—Purified by aniline fractionation followed by a treatment with bromine and distillation: 2 cc. of purified material was obtained; m. p., +2°; *n*, 1.4995; characteristic odor of benzene.

Component 93–95°.—Purified by fractional distillation: *d*, 0.744, *n*, 1.422; 1.06 double bond per C_7H_{14}. Hydrogenation and nitration gave a compound: b. p., 92–95°; *d*, 0.723; *n*, 1.4032, which contained hexahydrotoluene as an impurity. The physical constants are not in sufficient agreement with anything in the literature to allow a possible identification. The nearest physical constants given are for *d*-3-methylhexane: b. p., 92°; *d*, 0.687. The physical constants of the hydrogenated product show that it contained a large proportion of a paraffinic hexane, the boiling point of which corresponds to the one given for 3-methylhexane. Identification considered incomplete.

Δ^3-Tetrahydrotoluene.—B. p., 103°; *d*, 0.799; *n*, 1.443. Purified by fractional distillation: b. p., 102–103°; *d*, 0.791; *n*, 1.444; double bond, 1.08 per C_7H_{12}. Hydrogenation gave a compound, b. p., 100–102°; *d*, 0.7671; *n*, 1.4225. I. C. T. gives for methylcyclohexane: b. p., 100.8°; *d*, 0.764; *n*, 1.4235. Nitration failed to detect aromatic compounds.

Δ^2-Tetrahydrotoluene.—Not purified enough for identification; a sufficient intermediate persisted in the general distillation to suggest its presence.

Component 109–110°.—Purified by aniline fractionation: *d*, 0.783; *n*, 1.4413; double bond, 1.13 per C_7H_{14}. Hydrogenation and nitration indicated toluene as an impurity. Further purification of the saturated compound by fractional distillation gave a small quantity of hexahydrotoluene and of *iso*-octane: b. p., 116°; *d*, 0.706; *n*, 1.397. I. C. T. gives for *iso*-octane: b. p., 116°; d_4^{15}, 0.704; *n*, 1.3964.

Δ^1-Tetrahydrotoluene.—B. p., 111°; *d*, 0.809; *n*, 1.4496. Purified by fractional distillation: b. p., 110–111°, *d*, 0.818; *n*, 1.4653. Special test (Beilstein): 3 drops of sulfuric acid added to an alcoholic solution of the hydrocarbon gave a green color peculiar to Δ^1-tetrahydrotoluene. Double bonds, 0.75, indicating a large percentage of toluene. Hydrogenation and nitration yielded a large quantity of trinitrotoluene and hexahydrotoluene: b. p., 100°; *d*, 0.762; *n*, 1 423. I. C. T. gives for hexahydrotoluene: b. p., 100.8°; *d*, 0.764; *n*, 1.4235.

Toluene.—B. p., 110.5°; *d*, 0.866; *n*, 1.4962. Purified by aniline fractionation, treatment with bromine and steam distillation: b. p., 110° sharp; identified by its odor and nitration to mononitrotoluene, b. p., 220°, the latter also having a characteristic odor.

Component 121–122°.—*d*, 0.765; *n*, 1.4287; hydrogenation and nitration indicated the presence of a small amount of aromatic compounds and gave a material: b. p., 116–121°; *d*, 0.739; *n*, 1.4102; mol. wt., 112.4, indicating *iso*-octane with a small quantity of hexahydro-*m*-xylene as an impurity. A fraction 124–125° gave a hydrogenation product with a slightly higher boiling range, density and index of refraction, indicating another isomeric form of 2-methylheptene containing an increased quantity of hexahydro-*m*-xylene. Although the above two fractions were present in the distillation in sufficient quantity to indicate the presence of components, there was not enough for proper purification and identification; all indications were that they were isomeric methylheptenes, probably 2-methylheptenes, with the location of the double bond totally unknown.

Dihydro-*m*-xylene, Probably Δ-1,3.—No constants given in the literature. Purified by aniline fractionation: b. p., 129–130°; *d*, 0.795; *n*, 1.4451. Hydrogenation and nitration indicated the presence of a small quantity of xylene and of a compound, b. p., 122–129°, bulk at 125°; *d*, 0.764; *n*, 1.4208; mol. wt., 112.6. I. C. T. gives for

hexahydro-*m*-xylene: b. p., 123.7°; *d*, 0.771; *n*, 1.425; mol. wt., 112. These properties identify hexahydro-*m*-xylene with a small amount of paraffinic compounds as impurity. A substantial part of the original cut obtained by fractional distillation containing the dihydro-*m*-xylene was treated with bromine; no dibromides were found, only tetrabromides.

m-**Xylene.**—B. p., 139°; *d*, 0.865; *n*, 1.4973.—Purified by treating with an excess of bromine water, and steam distilling; redistilling several times to eliminate all traces of bromides gave a material, b. p., 137°; *d*, 0.866. Nitration to the trinitro compound gave white crystals melting sharply at 179.5°. Mulliken gives m. p. 180–181° for trinitro-*m*-xylene. It is thus shown that the xylene obtained was pure *m*-xylene containing no trace of either ortho or para derivatives.

p-**Tetrahydro-Ethyltoluene.**—Beilstein gives for the Δ^3-compound: b. p., 149°; *d*, 0.816; n^{16}, 1.453. Purified by fractional distillation: b. p., 144–145°; *d*, 0.813; *n*, 1.4529; double bond, 1.2 per C_9H_{16}. Hydrogenation and nitration gave a material: b. p., 147°; *d*, 0.784; *n*, 1.4335; mol. wt., 123. Beilstein gives for *p*-hexahydro-ethyltoluene: b. p., 147°; d_4^{15}, 0.788; n^{15}, 1.435; mol. wt., 126. There can be no question of the identification except for the position of the double bond, which may have been Δ^1 instead of Δ^3; no physical constants are available for the Δ^1-compound.

Component 158–159°.—*d*, 0.834; *n*, 1.4665; double bond, 0.998. Purified by fractional distillation; composition by combustion, $C_{10}H_{16}$, establishing the presence of a dicyclic compound. I. C. T. gives for thujene: b. p., 151°; *d*, 0.830; *n*, 1.4515. Hydrogenation and nitration gave a material, b. p., 158–161°; *d*, 0.813; *n*, 1.4498; mol. wt., 133.5–134.8 (theoretical for $C_{10}H_{18}$, 138); double bond, 0. Combustion gave $C_{10}H_{18}$ within 0.2%. Beilstein gives for thujane: b. p., 157°; *d*, 0.814–0.819; *n*, 1.4376–1.44395. Off-hand it would appear that the identification of the original material, as an isomeric form of thujene, was as definite as many of the foregoing identifications, but more careful consideration indicates that such is not the case. Identification by physical constants requires not only that the physical constants of the unknown be in close agreement with those of likely possibility, but that all, or nearly all, of the possibilities be known and listed, and that the constants are not in agreement with any of the other possibilities. This has been the case with all the components positively identified in C_5, C_6, C_7, C_8 and C_9, but it is not so with the dicyclic compound in C_{10}. It was therefore decided to consider the identification of this component as unestablished.

p-**Ethyltoluene.**—B. p., 162; *d*, 0.862; *n*, 1.4943. Purified by treating with bromine water and steam distilling: b. p., 160.5–163°; *d*, 0.866; *n*, 1.4832; mol. wt., 120.4, instead of 120, theoretical; saturated toward bromine; oxidation with permanganate yields terephthalic acid.

Component 162–163°.—*d*, 0.828; *n*, 1.46; mol. wt. 130.5; bromination indicated 1.0 double bond. Obtained only from rubber decomposed in the presence of magnesium. Hydrogenation and nitration gave a compound b. p., 162–164°; *d*, 0.794; *n*, 1.4407; saturated toward bromine; mol. wt., 135; combustion indicated a formula of $C_{10}H_{20}$ within 0.2%. This shows that the original material was of empirical formula $C_{10}H_{18}$. The hydrogenation was a quantitative check on the original bromination. It is evident that this is a single ring compound containing 1 double bond. It is impossible to identify this compound from any known data.

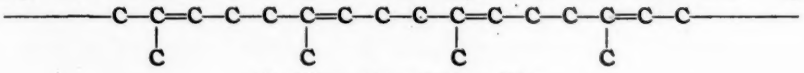
Component 162–163°.—The distillate from rubber alone gave a component in this boiling range: *d*, 0.8105; *n*, 1.456; double bond, 1.4. Aniline fractionation failed to purify it further. Thus it is seen that the distillation of rubber alone gives a lighter material than the distillation with magnesium and that the unsaturation is 1.4 instead of 1.0 double bond, indicating the presence of a dienic compound. If this density be extrapolated to 100% diene, 0.783 is obtained. By a separate synthesis,[7] a mixture of

[7] Midgley and Henne, THIS JOURNAL, **51**, 1294 (1929).

2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes was obtained, the physical constants of which were: b. p., 163–164°; *d*, 0.773. Considered as not a positive identification, but as strong evidence that a dimethyloctadiene was present.

Dipentene.—B. p., 176°; d^{18}, 0.865; *n*, 1.471. The density given by I. C. T. is apparently an error; Schimmel and Company give 0.844; Brühl gives $d_4^{20.85}$, 0.8402; Staudinger, d^{20}, 0.841. Purified by fractional distillation: b. p., 176°; *d*, 0.8435; *n*, 1.4712; double bonds, 1.96. Hydrogenation gave *p*-menthane: b. p., 170–171.2°; *d*, 0.796; *n*, 1.4387. I. C. T. gives for *p*-menthane: b. p., 170°; *d*, 0.793; *n*, 1.437. No evidence was obtained of the presence of myrcene, or a terpene, b. p., 168–169°, or of dimethylbutadiene.[4]

Derivation of the Structural Formula of the Products from That of Rubber.—Prior to entering upon this investigation, a method had been developed for illustrating the mechanism by which isoprene and dipentene form during destructive distillation. After the above results were obtained, it was felt that the method should be extended to include as many of the products as possible. A relatively simple solution is herewith presented which completely covers a majority of the cases, a few partially, and leaves only the formation of benzene without explanation. The long-chain structural formula for rubber hydrocarbon[8] is broken at single



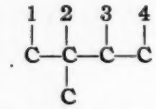
Staudinger formula for rubber

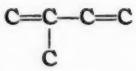
valences to give a section containing a given number of carbon atoms. The points of breakage are represented by partial valences and the double bonds are resolved into partial valence form. This is called the *transient form*. The following postulates are then observed: (1) adjacent partial valences may join to form double bonds (Thiele); (2) single partial valences six carbons apart may join to form rings; (3) any pair of partial valences may accept hydrogen, preferably those not adjacent to others; (4) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic compounds; (5) partial valences not joining nor accepting hydrogen may migrate.

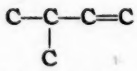
After having derived all of the combinations by applying the above assumptions to a transient form, the resulting *stable* forms are examined and those forms cast out which experimental data show do not form by pyrolytic decomposition. Predominant among these are molecules containing a carbon atom in a ring bonded to two other carbon atoms external from the ring and those containing a methylene group attached to a ring. The formation of dienic compounds has been disregarded, since no experimental data were obtained.

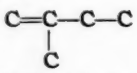
The mechanism of the reactions involving 5 carbon atoms (called compounds in C_5 for simplicity) may be represented as follows:

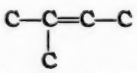
[8] Staudinger, *Ber.*, **44**, 2212 (1911); **46**, 2466 (1913); *Helv. Chim. Acta*, **5**, 743 (1922); **5**, 756 (1922); **5**, 785 (1922); *Ber.*, **57**, 1203 (1924); *Helv. Chim. Acta*, **7**, 842 (1924); *Z. angew. Chem.*, **38**, 226 (1925).


Transient form in C_5


Isoprene

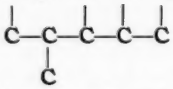

3-Methyl-1-butene

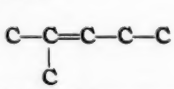

2-Methyl-1-butene

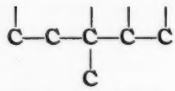

2-Methyl-2-butene

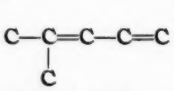
Because of the preponderance of isoprene(C_5), dipentene(C_{10}) and heveen(C_{15}) in the products of destructive distillation, it is held certain that the single bond furthest removed from the double bonds is the most easily broken by pyrolysis. The same conclusion is arrived at by C. D. Hurd, starting from purely theoretical considerations,[9] and is found to hold when the other pyrolysis products of rubber are examined. Hence the transient form shown above predominates in C_5 to the practical exclusion of the two other possible forms. Four stable forms are derived from it: isoprene by the joining of 1 with 2 and 3 with 4, 3-methyl-1-butene by the acceptance of hydrogen on 1 and 2 and the joining of 3 with 4 and 2-methyl-1-butene by the acceptance of hydrogen on 1 and 4 and the joining of 2 with 3. Isoprene predominates, since it requires no hydrogen to produce a stable form.

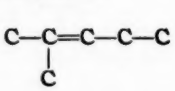
In C_6, two transient forms are possible. Each case requires that a bond adjacent to a double bond be broken. The proportion of C_6 compounds should therefore be small. In neither case does a stable form result without either migration or hydrogen acceptance.


Transient form No. 1 in C_6

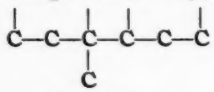

2-Methyl-2-pentene

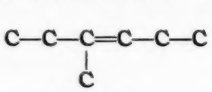

Transient form No. 2 in C_6


3-Methyl-1,3-pentadiene


3-Methyl-2-pentene

There is only one transient form possible in C_7. It requires the breaking of two single bonds adjacent to double bonds. It is obvious that valences


Transient form in C_7


3-Methyl-3-hexene

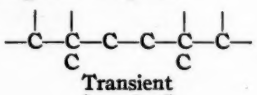
Δ^1-Tetrahydrotoluene

Toluene

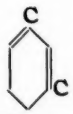
[9] C. D. Hurd, "The Pyrolysis of Carbon Compounds," American Chemical Society Monograph Series, The Chemical Catalog Co., New York, 1929.

1 and 6 may either accept hydrogen to form 3-methyl-3-hexene or join to form Δ^1-tetrahydrotoluene, the dehydrogenation of which gives toluene.

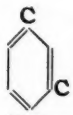
C_8 exhibits the possibility of only one transient form and in a similar manner to C_7 partial valences 1 and 6 may either hydrogenate to form a dienic compound or join to form dihydro-*m*-xylene, the dehydrogenation of which gives *m*-xylene.



Transient form in C_8

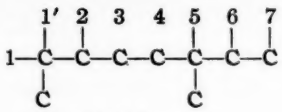


Dihydro-*m*-xylene



m-Xylene

C_9 again presents two possible transient forms. The only evidence obtained covering the many possibilities in C_9 was in connection with transient form 1, which appeared to accept hydrogen by 1 and 1′, 2 joining with 7 and 5 with 6. The dehydrogenation of the resulting tetrahydro-*p*-ethyltoluene yields *p*-ethyltoluene. Other ring forms suggested as possible products of transient form 1 or 2 could not be detected.

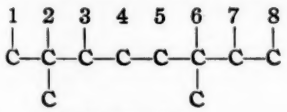


Transient form No. 1 in C_9

Tetrahydro-*p*-ethyltoluene

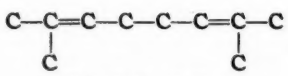
p-Ethyltoluene

In C_{10}, as in C_5, three transient forms are possible, but since one of them is obtained by the rupture of only weak bonds, it should be predominant; it stabilizes without migration or hydrogenation by the joining of 3 with 8, 1 with 2 and 6 with 7, giving dipentene. By accepting hydrogen in 1,8 it stabilizes to dimethyloctadiene.



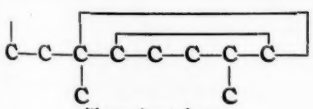
Predominating transient form in C_{10}

Dipentene



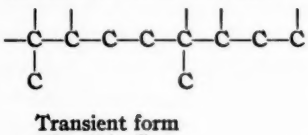
Dimethyloctadiene

The other transient forms present an interesting speculation in connection with the component 158–159° (shown to be a dicyclic compound



Transient form No. 2 in C_{10}

Isomeric thujene



Transient form No. 3 in C_{10}

Component 162°?

$C_{10}H_{16}$), and component 162–163° (shown to be a single ring compound $C_{10}H_{18}$). The development from transient form 2 serves as a suggestion of the mechanism of the formation of a dicyclic compound, while the development from transient form 3 is a suggestion, predicated on the behavior of form 1 in C_9, to show the acceptance of hydrogen and subsequent ring formation. Both derivations are only speculations. If these suggestions could be proved experimentally, an interesting generality might be derived, namely, that when a terminal carbon atom has two partial valences attached to it, dicyclic ring formation is favored, but when an internal carbon is in the same case, hydrogen acceptance is favored.

The identification of Δ^3-tetrahydrotoluene and the evidence for the existence of Δ^2-tetrahydrotoluene among the products is not predictable. It is felt, however, that migration of the double bond from the Δ^1-position should not be considered as unlikely, since the amounts of Δ^2- and Δ^3-compounds were exceedingly small.

Discussion

In view of the evidence at hand, it can scarcely be doubted that with the exception of benzene the compounds of the aromatic series present were all derived by dehydrogenation of the corresponding hydro-aromatic forms, since only those aromatic compounds are found whose hydro-derivatives are also present. Dihydro-*m*-xylene is the only predictable ring compound in C_8, hence if dehydrogenation occurs, only *m*-xylene should result. If, on the other hand, *m*-xylene is a primary pyrolysis product, small amounts of the ortho and para derivatives at least should be present. Particular care was taken to ascertain that no other xylene was present than the meta derivative. The same reasoning holds true in C_9 with respect to *p*-ethyltoluene. A reason for the dehydrogenation during destructive distillation is not apparent. It is well known that cyclohexane in the presence of nickel and at similar temperatures will dehydrogenate to benzene, but there was no catalyst present to account for a similar behavior during pyrolysis of rubber alone. It is significant that the presence of magnesium in the rubber increases decidedly the proportion of aromatic compounds.

The origin of benzene is obscure. It is not due to accidental contamination in the laboratory, since the presence of a metal in the rubber always increases the amount of benzene in the distillate. Extreme pyrolysis in locally overheated spots might account for its formation.

To sum up, of the 23 compounds identified, 12 were in perfect agreement with the postulated results, 5 were in agreement as far as their identification was possible and rational explanations of the other 6 are not at variance with the postulates. In C_5 all forms predicted were obtained, in C_6, C_7, and C_8 chain compounds only were missing from the

predictions. In C_9 the only logical rings were obtained, in fact, and in C_{10} all normal predictions were fulfilled.

Relationship of the Results to the Structural Formula of Rubber.—The constitution of the ten-carbon section of rubber has been thoroughly established by oxidation and confirmed by many investigators, but assemblage of these units into the complete structural formula of rubber has been the basis of much work and argument. Harries originally interpreted the results of his oxidations as indicating the existence of an eight-sided ring. He was more or less driven from his original interpretation in later years. Staudinger and co-workers[4,8] support a long-chain structure in which the ten carbon atom sections recur and are bonded together by ordinary valences, thus requiring no residual valences to account for the structure. Many intermediate speculations have been indulged in.

The results of this investigation throw no additional light upon the discussion. The use of the long-chain formula affords greater ease for interpretation, but the results do not contradict Harries viewpoint. Recently, E. A. Hauser[10] has supported the hypothesis that the rubber molecule is a long chain arranged in helix form, by interpreting the x-ray pattern of stretched rubber. The predominant formation of six-sided rings in C_7, C_8, C_9 and C_{10} appears to support this hypothesis, since to account for ring formation upon any other arrangement that has been advanced requires the joining of partial valences across the space occupied by six carbon atoms, whereas a helix may be so arranged that the carbon atoms, six apart in the chain, may be adjacent in space.

Conclusions

All of the products of the destructive distillation of natural rubber are directly derived, by simple reactions, from the rubber molecule. Those compounds predominate which represent sections of the rubber molecule occurring between the single bonds furthest removed from the double bonds.

Summary

Two hundred pounds of pale crepe rubber have been destructively distilled at atmospheric pressure. The distillate was fractionated and its components identified from C_5 to C_{10}, as shown in the table. Assuming that the Staudinger formula is correct, that the single bonds furthest from the double bonds are the weaker spots and that the formation of six-carbon rings is favored, it has been shown that nearly all of the compounds actually isolated could be predicted. The experimental results, together with forthcoming experimental data, are expected to be used to throw light upon the formula of the rubber molecule.

ITHACA, N. Y.

[10] E. A. Hauser, address at the Swampscott Meeting of the American Chemical Society, September, 1928.

[Reprinted from the Journal of the American Chemical Society, Vol. 51, No. 4, page 1293. April, 1929.]

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. II. REDUCTION OF ISOPRENE BY $Na-NH_3$

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

The reduction of isoprene by sodium in liquid ammonia was attempted to determine: (1) whether reduction would take place in preference to polymerization and (2) the location of the added hydrogen.

Isoprene was added to sodium dissolved in liquid ammonia and a 60% yield of 2-methyl-2-butene resulted. No other volatile hydrocarbon was found. High molecular weight hydrocarbons were formed but were not investigated. It is thus shown: (1) that the predominant reaction proceeds in accordance with the equation $C_5H_8 + 2Na + 2NH_3 = C_5H_{10} + 2NaNH_2$ and (2) that hydrogen adds to isoprene in the 1,4-position, in agreement with Thiele's theory.

The hydrogen addition is similar to the bromination of isoprene at low temperature.[1] If properly conducted the latter reaction stops after 2 atoms of bromine have been added to 1 molecule of isoprene; the resulting compound, 1,4-dibromo-2-methyl-2-butene, is characterized by the inactivity of its double bond toward bromine. Similarly, 2-methyl-2-butene obtained by reduction of isoprene is not reduced to *iso*pentane by an excess of $Na-NH_3$ reagent.

Procedure.—750 cc. of liquid ammonia are placed in a one-liter round-bottomed flask (Pyrex) and 46 g. of sodium are dissolved in it. The flask is equipped with a rubber stopper carrying a separatory funnel and an abduction tube. One mole of isoprene is slowly dripped into the liquid: the stem of the separatory funnel should nearly reach the surface of the ammonia in order to prevent abduction of isoprene by the escaping ammonia vapors. When the isoprene drops strike the ammonia, a clear sound is heard which can be used to regulate the delivery. The ammonia vapors carry the reduced hydrocarbon, together with a small quantity of unchanged isoprene, through an empty safety bottle to a cylinder filled with cracked ice. Ammonia dissolves immediately, the ice melts, and the water flows into a large separatory funnel; the hydrocarbon, which condenses on the ice, is carried with the water and collects as an upper layer in the separatory funnel. By rerunning, the hydrocarbon can be completely freed of isoprene.

ITHACA, NEW YORK

[1] Staudinger, *Helv. Chim. Acta*, **5**, 756–67 (1922).

[Reprinted from the Journal of the American Chemical Society, Vol. 51, No. 4, page 1294. April, 1929.]

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. III. DIMETHYLOCTADIENE

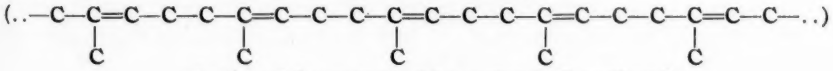
BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

RECEIVED DECEMBER 7, 1928 PUBLISHED APRIL 5, 1929

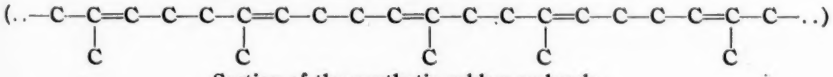
The polymerization of isoprene to synthetic rubber has long been known. The mechanism of this reaction has, however, so far escaped detection. To throw light upon this question, it was decided to polymerize isoprene in the presence of active hydrogen, with the hope that polymerization might be stopped at the dimer stage. This was accomplished in the following manner.

Well-purified isoprene, active toward polymerization, was placed in contact with metallic potassium chips and ethyl alcohol slowly added at a rate just sufficient to give a moderate evolution of hydrogen at the surface of the potassium. A good yield of a light yellow oil resulted, which upon analysis proved to be a mixture of 2,6-, 2,7- and 3,6-dimethyl-2,6-octadienes. These isomers are the dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- or the 1,1-carbon atoms, respectively, and the addition of hydrogen to the 1,8-positions of the dimer. No trace of a compound of cyclic nature could be detected.

These results suggest that the polymer of isoprene produced by contact with alkali metals and called "sodium rubber" (the commonest of the synthetic rubbers) is a long chain formed of isoprene units linked together by means of their 1 and 4 carbon atoms. This chain very closely resembles the long-chain structural formula of natural rubber proposed by Staudinger[1] and his associates, except that the recurring methyl groups may be placed at either side of the double bond, thus



Section of the natural rubber molecule (Staudinger)



Section of the synthetic rubber molecule

It should be noted that in the natural product the groups attached to each double bond may be expected to present always the same *cis*- or *trans*-configuration, while such uniformity can hardly be hoped for in the synthetic product.

The products of the side reactions appear to be high polymers; their constitution is being studied at the present time. It is thought that a small

[1] Staudinger, *Helv. Chim. Acta*, **5**, 785–805 (1922), and later papers.

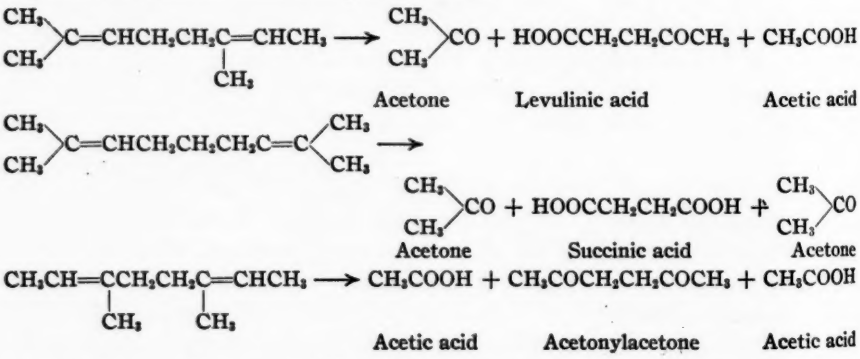
amount of 2-methyl-2-butene was formed during the reaction but it was lost with the escaping hydrogen excess.

Procedure.—The apparatus comprises a 500-cc. round-bottomed flask equipped with a reflux condenser and a separatory funnel. The top of the condenser is connected to a glass tube whose end dips into a test-tube containing a little alcohol, thus making it possible to judge the rate at which hydrogen escapes.

Two-gram molecules of isoprene were placed in the flask, 4-g. atoms of potassium shavings quickly added and the flask connected to the condenser and separatory funnel; alcohol was dripped in at such a rate that a hydrogen excess escaped slowly from the apparatus. During the reaction the potassium remained shiny; when it was completely used, the potassium ethylate formed during the reaction was decomposed by adding water slowly through the separatory funnel. The reaction product was decanted, washed, dried, and distilled. The mixture of dimethyloctadienes had the following constants: b. p., 163–167°; d_{20}^{20}, 0.769; n_D^{20}, 1.4457; mol. wt., 136.8 (138, theoretical). The bromination number determined with a $KBrO_3$–KBr mixture gives 2 double bonds per $C_{10}H_{18}$. Combustion checks the previous formula. Hydrogenation requires 2 moles of hydrogen and yields 2,6-, 2,7- and 3,6-dimethyloctanes.

Analysis of the Dimethyloctadienes.—The hydrocarbon was oxidized by means of a solution of CrO_3 in acetic acid. After removal of the bulk of Cr_2O_3 as $Cr_2(SO_4)_3$, insoluble in H_2SO_4, the following products were detected: acetone, 2,5-hexanedione, levulinic acid, and succinic acid. These compounds are all very easily characterized: acetone by means of its mercury compounds, acetonylacetone by its dioxime and its unusually strong reaction with bromine, levulinic acid by its reaction with sodium nitroprusside and succinic acid by the pyrrole–pine shaving reaction.

The following diagram compares the oxidation products with the hydrocarbons from which they are formed.



Although one of the oxidation products probably was acetic acid, it is obvious that it could not be detected, since the oxidation was carried

out in an acetic acid solution. It is nevertheless evident that the hydrocarbon obtained by polymerization and simultaneous reduction of isoprene is a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes.

Summary

The dimer of isoprene formed under conditions which normally produce "sodium rubber" has been stabilized by the addition of hydrogen. This partially hydrogenated dimer is a mixture of three isomeric dimethyloctadienes; its formation indicates that the mechanism of the polymerization of isoprene to synthetic rubber is the joining of many isoprene molecules by linkage of the 1,1-, the 1,4- or the 4,4-carbon atoms to produce a long-chain molecule.

ITHACA, NEW YORK

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 4, page 316. April, 1929.]

Effect of Antioxidants in Typical Rubber Stocks[1]

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A NUMBER of valuable papers have appeared from time to time concerning the use of antioxidants in rubber goods. In most of these papers tensile strength and elongation before and after varying periods of aging in the Geer oven[2] or the Bierer-Davis bomb[3] have been the criterion of merit of different antioxidants. Recognizing the value of these tests, the writer wishes to point out certain additional evidence of the usefulness of antioxidants in the rubber industry as shown by other tests as well as by tensile strength and elongation.

While antioxidants are of value in a great variety of rubber goods, only a few typical examples are given as illustrating the effects of antioxidants in factory production stocks—namely, tire treads, inner tubes, dry-heat-cured goods, specification stocks, and sponge rubber. In these examples Age-Rite resin was the antioxidant used, since this was the first non-accelerating antioxidant available for use in this plant. After nearly five years of production use, a sufficient background of experience has been obtained to judge the value of this antioxidant in practice. Where available, natural aging results are presented along with artificial aging results.

Tire Treads

The effects of 1 per cent of antioxidant on the recipe in a blooming tread stock are shown in Table I. The stocks used in these tests were mixed and cured in the laboratory, making press sheets $15 \times 20 \times 0.25$ cm. ($6 \times 8 \times {}^{3}/_{32}$ inch). The cure was controlled to approximate the actual heat treatment that a tread using the same compound received in the factory.

[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Geer and Evans, *Rubber Age (London)*, **2**, 308 (1921).

[3] Bierer and Davis, IND. ENG. CHEM., **16**, 711 (1924).

Strips of these stocks were aged in the Geer oven, in sunlight, and in dark boxes in a storeroom. In the sunlight one set of strips was exposed without tension at 45 degrees from the horizontal, facing south, during June to September, 1924. Another set of strips was flexed while exposed to sunlight. After 3 weeks' flexing in sunlight the stock containing antioxidant showed slight surface cracks, while the stock without antioxidant was cracked much worse.

Sections of two 30 × 3½ inch tires were obtained. One using the above tread compound without antioxidant was cured in November, 1923. The other section was cured in February, 1924, and carried a tread compound the same except for the substitution of 0.44 part antioxidant for an equal weight of rubber in 100 parts of stock. Other conditions of manufacture and storage were identical. After nearly three years of storage in a fairly dark sample room, the stock without antioxidant was weak as shown by "bite" and hand tests. The stock containing antioxidant was markedly stronger. After nearly five years of storage the difference between the two stocks was even greater.

Antioxidants have shown a similar effect in maintaining resistance to tear when aged in the Geer oven and in the Bierer bomb, or in storage in the dark. Abrasion tests after varying periods in the Geer oven have shown the lasting properties of tread stock to be better when containing antioxidant.

Table I—Effect of Antioxidants on Tire Tread Stock

Rubber 53, zinc oxide 15, gas black 20, and sulfur 3 per cent
Accelerator—hexamethylenetetramine

Treatment	No Antioxidant			1% Antioxidant		
	Tensile strength		Elongation at break	Tensile strength		Elongation at break
	Kg./ sq. cm.	*Lbs./ sq. in.*	%	*Kg./ sq. cm.*	*Lbs./ sq. in.*	%
Original	250	3550	690	254	3610	700
Geer oven 7 days	87	1240	440	167	2380	560
Geer oven 14 days	49	700	240	87	1240	430
Sunlight 6 weeks	208	2960	600	232	3300	670
Sunlight 10 weeks	177	2520	570	221	3150	610
Sunlight 14 weeks	159	2260	530	216	3070	560
In dark 2 years, 5 months	184	2620	520	219	3120	570

Inner Tubes

In high-gum inner tubes tensile strength is probably not so important as resistance to tear. Inner tubes 29 × 4.40 inches were made up in the factory from two stocks identical except that in one case 0.75 part of antioxidant was substituted for an equal part of rubber in 100 parts of the compound, while the other stock contained no antioxidant. One tube of each compound was run approximately 2000 miles on the dynamometer and tested. Tear was determined on crescent-shaped strips having nicks cut on the concave side. Jaws were

fastened to the ends of the crescent and were separated at the rate of 50.8 cm. (20 inches) per minute. The figures represent pounds per 0.1 inch thickness and are averages of transverse and longitudinal tear. The results of these tests are shown in Table II. It is noteworthy that resistance to tear after running on the dynamometer decreased when antioxidant was not used.

Table II—Blooming Inner Tube (80 Per Cent Rubber)

Treatment	No Antioxidant				0.75% Antioxidant			
	Tensile strength		Elongation at break	Tear	Tensile strength		Elongation at break	Tear
	Kg./ sq. cm.	*Lbs./ sq. in.*	%		*Kg./ sq. cm.*	*Lbs./ sq. in.*	%	
Original-new tube	147	2090	730	19.2	161	2290	750	18.5
Original-used tube	153	2180[a]	715[a]	13.4[a]	170	2420[b]	695[b]	18.6[b]
Geer oven 4 days[c]	129	1840	665	6.8	165	2350	700	16.1
Geer oven 7 days	119	1690	600	5.7	167	2370	700	9.1
Geer oven 10 days	95	1360	565	5.0	185	2630	620	7.8
Geer oven 14 days	53	750	465	3.7	165	2350	605	7.4
2 days oxygen bomb, 70° C., 300 lbs. per sq. in. (21 kg. per sq. cm.)	43	610	475	..	172	2440	695	..
4 days oxygen bomb, 70° C., 300 lbs. per sq. in.	...	..	...	..	92	1300	600	..

[a] Tube run 2113 miles on dynamometer.
[b] Tube run 1857 miles on dynamometer.
[c] All oven and bomb tests are on tubes run on dynamometer.

Stocks Cured in Dry Air

Much footwear and a number of specialty stocks are cured in dry air. It is often a very difficult problem to get stocks to cure properly in dry heat without becoming tacky and at the same time not to cure so quickly as to scorch in handling. This surface tack in dry-heat cures is due to oxidation, since it does not occur in steam cures or cures in dry carbon dioxide. Surface tack is greatly diminished or eliminated by the proper use of antioxidants, especially AgeRite resin. Many stocks now in use could not be handled without antioxidant. Antioxidants also greatly improve resistance to cracking when flexed in sunlight.

Specification Stocks

In many rubber goods artificial aging specifications are imposed. In these cases antioxidants have proved to be of considerable value, often permitting the use of cheaper compounds. The amount of antioxidant to be used in these cases must be determined by the nature of the specifications. In certain cases a minimum acetone extract is specified which will not permit the use of more than a very small amount of antioxidant. A steam hose cover was considerably improved, as indicated by the rack test, by the addition of 0.5 per cent antioxidant on the recipe.

Sponge Rubber

A very spectacular example of the value of antioxidants was in black sponge rubber. Samples were taken from factory production, both before and after substitution into the recipe of 0.5 per cent of antioxidant for an equal amount of rubber. These samples were aged in the Bierer bomb at 70° C. and 300 pounds per square inch (21 kg. per sq. cm.) oxygen pressure for two days. Without antioxidant the sponge became so brittle in some places it could not be bent without cracking, while the sample with antioxidant was quite live and flexible. Similar results were obtained with a poorer grade of sponge rubber made in the laboratory and stored in the dark without artificial aging tests.

Effect of High Temperatures

In order to get some measure of the value of antioxidants in stocks subjected in service to high temperatures in the presence of air, a 90° C. air oven test was investigated. Since a short heating at a very high temperature is known to depolymerize or otherwise adversely affect rubber, it was thought that perhaps long heating at 90° C. might produce the same effect. A day in air at 90° C. was found to cause nearly as much deterioration of rubber as a week in air at 70° C. Aging at 90° C. in an oven through which commercial nitrogen was passed gave in several trials almost the same results as aging in air at the same temperature. If, however, the strips were sealed in vacuum or in a small container in purified nitrogen, very little deterioration took place. While long heating at 90° C. in the absence of oxygen produces overcure in some stocks, heating in the presence of air or an inert gas containing a very small concentration of oxygen causes vastly more deterioration.

Table III—Effect of Heat and of Oxygen on Tire Tread Stock
Rubber 53, zinc oxide 15, gas black 20, and sulfur 3 per cent
Cured 45 minutes at 146° C. in press
Accelerator—hexamethylenetetramine

Treatment	No Antioxidant			0.5% Antioxidant on Recipe		
	Tensile strength		Elongation at break	Tensile strength		Elongation at break
	Kg./ sq. cm.	*Lbs./ sq. in.*	%	*Kg./ sq. cm.*	*Lbs./ sq. in.*	%
Original	269	3830	633	262	3730	633
7 days in vacuum at 90° C.	238	3380	530	241	3430	565
2 days in commercial nitrogen at 90° C.	77	1100	353	102	1450	423
2 days in air at 90° C	71	1010	300	99	1410	400
7 days in Geer oven at 70° C.	133	1890	473	190	2700	562

In the stocks tested, and probably in all well-balanced stocks that are not highly accelerated, the effect of temperatures up to 90° C. in the absence of oxygen is insignificant as compared

with the effect of oxygen at these temperatures. Similar results have been reported by Jones,[4] who found that three typical rubber stocks showed almost no change in tensile strength and elongation in 2 weeks at 70° C. in a vacuum but were markedly deteriorated after the same period in air at 70° C.

Table IV—Effect of Heat and of Oxygen on High Zinc Oxide Tube Stock

Rubber 48, zinc oxide 45, and sulfur 2 per cent
Accelerator—hexamethylenetetramine

Treatment	No Antioxidant			1.5% Antioxidant		
	Tensile strength		Elongation at break	Tensile strength		Elongation at break
	Kg./sq. cm.	*Lbs./sq. in.*	%	*Kg./sq. cm.*	*Lbs./sq. in.*	%
Original	197	2800	620	198	2810	603
7 days pure nitrogen at 90° C.	190	2700	593	198	2810	600
2 days in air at 90° C.	168	2390	653	215	3060	660
3 days in air at 90° C.	138	1960	627	193	2750	637
4 days in air at 90° C.	98	1390	580	165	2340	633

The effect of air at 70° C. and of air, commercial nitrogen, and vacuum at 90° C. on a tread stock with and without antioxidant is shown in Table III. Deterioration in 2 days in commercial nitrogen or air at 90° C. was very great. Seven days at 90° C. in vacuum caused only a slight overcure.

The effects of purified nitrogen in a sealed flask and of air at 90° C. in a high zinc oxide tube stock, both without and with 1.5 per cent antioxidant on the recipe, are shown in Table IV. Results of similar tests with a low zinc oxide tube stock are shown in Table V, in which 2.5 per cent antioxidant on the recipe was used.

Table V—Effect of Heat and of Oxygen on Low Zinc Oxide Tube Stock

Rubber 82, zinc oxide 15, sulfur 2.3, and di-*o*-tolylguanidine 0.5 per cent

Treatment	No Antioxidant			2.5% Antioxidant		
	Tensile strength		Elongation at break	Tensile strength		Elongation at break
	Kg./sq. cm.	*Lbs./sq. in.*	%	*Kg./sq. cm.*	*Lbs./sq. in.*	%
Original	225	3200	730	226	3220	760
7 days pure nitrogen at 90° C.	209	2970	625	219	3120	613
2 days in air at 90° C.	179	2550	773	230	3270	735
3 days in air at 90° C.	134	1900	710	212	3010	730
4 days in air at 90° C.	72	1030	663	197	2800	740

Conclusion

The results of these tests show that antioxidants are of value in stocks which become hot in service, such as bus tubes, belt frictions, and heavy truck tire treads. It is believed that aging at 90° C., both in air and in an inert gas free from oxygen, will be of assistance in separating the factors of oxi-

[4] Jones, Ind. Eng. Chem., **17**, 871 (1925).

dation and overcure in designing rubber compounds for resistance to heat.

Acknowledgment

The writer wishes to express his appreciation to friends for the use of data, and particularly to H. A. Winkelmann for results on sunlight and Geer oven aging on tread stocks.

[Reprinted from Analytical Edition of Industrial and Engineering Chemistry, Vol. 1, No. 2, page 106. April 15, 1929.]

A Temperature-Recording Micropress for Studying the Course of Vulcanization[1]

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A new temperature-recording, electrically heated micropress for use in connection with the microscopical observation of vulcanization is described. This instrument permits the duplication of press cures on a small scale and renders it possible to determine the temperature at which various changes take place during cure.

The vulcanization of several non-sulfur mixtures is studied, certain differences in behavior being noticed between this type of cure and that of mixtures containing sulfur.

A SURVEY of the extensive literature on the nature of vulcanization reveals the fact that, almost without exception, work on this problem has been confined to purely analytical methods of attack. This classical chemical procedure shows only the final result of vulcanization—that is, the sum of all changes that have taken place—and thus ignores changes in the degree of dispersion, an inversion of phases, and other changes which may be of fundamental importance but which cannot be detected by the older chemical methods.

Microscopic investigation, on the other hand, offers a new method of attack, with many possibilities, inasmuch as it

[1] Presented under the title "Microscopical Observations on the Vulcanization of Sulfur-Free Rubber Compounds" before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

permits observation of the progressive changes that take place throughout the vulcanizing process and leads to a better knowledge of colloidal changes, which may in themselves be sufficient to explain vulcanization. Weber[2] was the first to recognize the insufficiency of analytical methods, and he introduced the microscope in the study of the blooming of sulfur. This technic was later utilized by Breuil,[3] Loewen,[4] and Regnaud.[5] All these investigators first heated their samples in an oven and then subjected them to microscopical examination; hence no simultaneous curing and microscopical observation was possible.

It was only during the past year or so that further work was done along this line by Hauser and by Dannenberg. The micropress developed by Hauser[6] employs steam as the heating medium. In this equipment the temperature of the sample is found from the temperature-pressure relation of saturated steam, and accordingly this apparatus can only be used for work above 100° C. Since the press was designed for curing at one definite temperature, it is not adaptable to temperature measurement where the temperature is rapidly changed. Dannenberg[7] devised an electrically heated micropress which permits the examination of the sample throughout the curing operation. With this equipment the temperature of the sample is found by inserting a thermometer in a small hole in the apparatus midway between the heating coil and the sample. Because of the location of the thermometer and because no account is taken of such factors as rate of heating and radiation and convection losses, this method of measurement does not give the true temperature of the sample.

The ideal equipment for microscopic vulcanization would be one which, first, would permit the accurate recording of the temperature of the sample over a range of 30° to 170° C., and in which, second, the sample could be kept at any desired temperature.

The micropress described below utilizes a thermocouple to measure the temperature of the sample and thus fulfils both of the requirements outlined above.

Description of Micropress

The micropress, shown in modified cross section in Figure 1, consists of three parts: the top portion, *A*, around which the chromel heating coil is wound, the middle member, *B*, in which the thermocouple is incorporated, and the bottom part, *C*, which holds the sample.

The top part is shaped like an annular ring and is grooved on the outside to permit the winding of the chromel resist-

[2] Weber, "Chemistry of India Rubber," p. 110, London, 1919.
[3] Breuil, *Caoutchouc*, **2**, 82, 118, 158, 197 (1905).
[4] Loewen, *Gummi-Ztg.*, **27**, 1301 (1913).
[5] Regnaud, *Chimie et industrie*, **18**, 93T (1927).
[6] Hauser, "Colloid Symposium Monograph," Vol. VI, p. 207 (1928).
[7] Dannenberg, *Kautschuk*, **3**, 104, 128 (1927).

ance which constitutes the heating coil. In order to show more clearly the construction of the apparatus, it has been drawn without the asbestos lagging, which in practice covers the top and side of the member *A* in order to confine the heat and to protect the objective of the microscope.

The middle member, *B*, is cup-shaped to permit the focusing of the microscope on the sample. A thermocouple is incorporated in this member by inserting an iron and a constantan wire in this member so that their ends are just flush with the metal surface which fits over the sample.

The bottom section, *C*, is recessed to receive the sample, which is placed between a circular slide and cover glass. A small hole is bored through both bottom and middle members in order to allow the light from the condenser to pass through the sample and up into the microscope.

It is evident that the middle member, which is made of mild steel and has inserted in it an iron and a constantan wire, acts as the hot junction of the thermocouple. Both wires are insulated and attached to the terminals of a millivoltmeter, 0 to 10 millivolts range, which act as the cold junction of the couple.

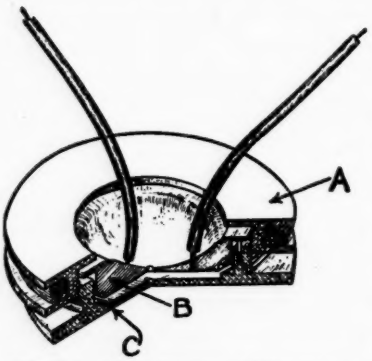

Figure 1—Cross Section of Micropress

The thermocouple as constructed records the temperature of only that part of the hot junction exposed to the air, and since this is far from the temperature of the sample it was necessary to calibrate it. This was done by placing organic crystals of known melting point between a slide and cover glass in the same position as the rubber sample. Current was applied to the heating coil and the melting of the crystals was observed microscopically, the millivoltmeter reading being taken at the time the crystals melted. A number of crystals of wide melting range were used in the calibration and a curve was determined for the temperature range usually encountered in vulcanization—viz., 30° to 170° C.

In using the apparatus, the sample is placed between a circular slide and cover glass and is placed in the recess in the bottom member. The middle portion is next put in position over the sample and the bottom screwed into the top member. These parts are screwed together until the sample is compressed or squeezed out sufficiently thin to permit light from the condenser to pass through the sample.

Curing Agent

Most of the work done in the study of vulcanization has

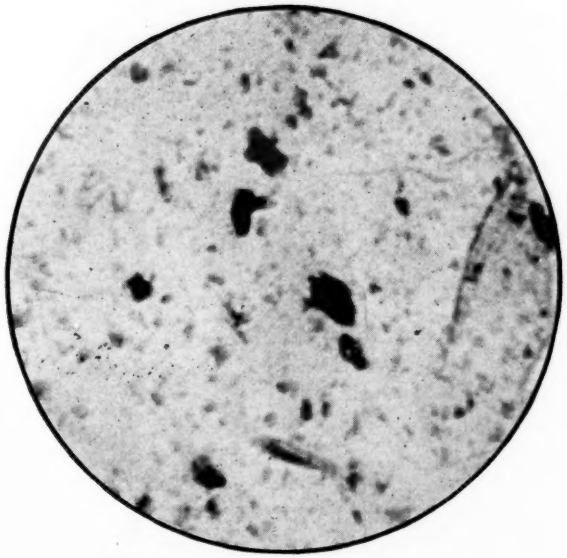

Figure 2—Mixture II before Cure. 750 ×

Figure 3—Mixture II Heated. 750 ×

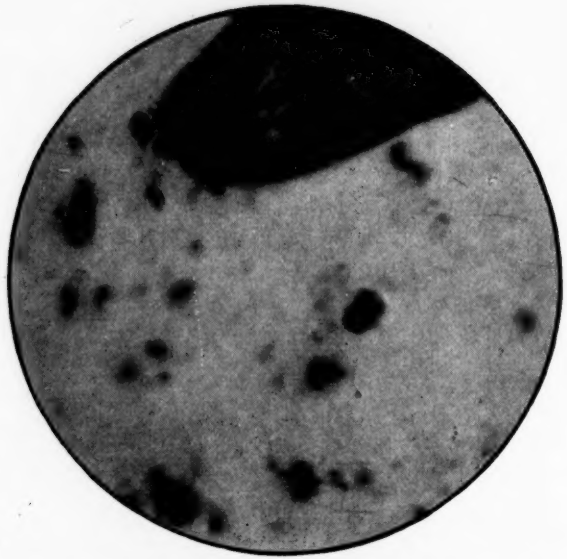

Figure 4—Mixture II after Cooling Following Cure. 750 ×

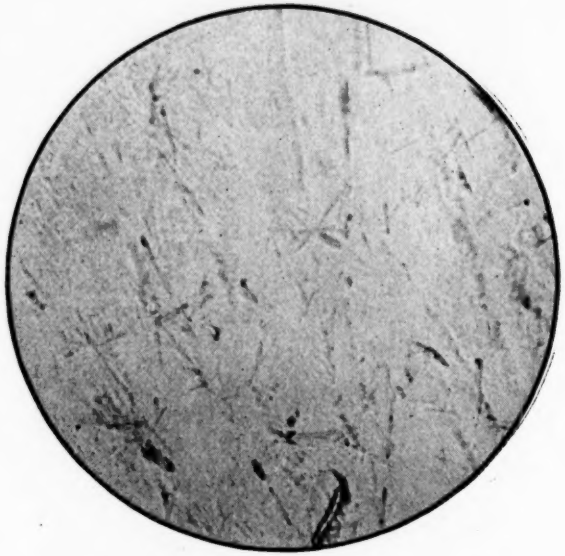

Figure 5—Mixture IV before Cure. 750 ×

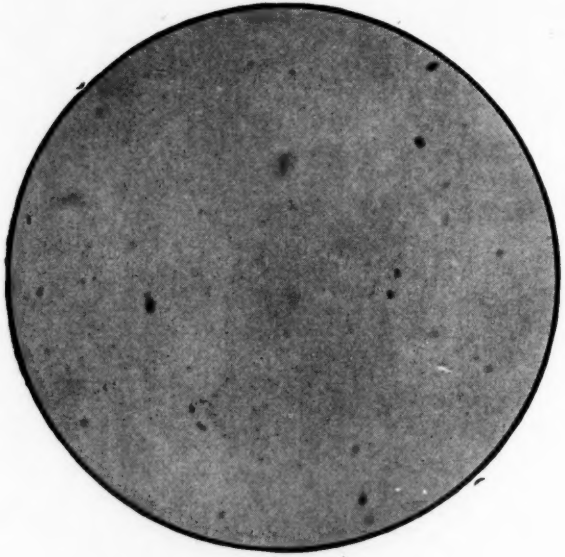

Figure 6—Mixture IV Heated. 750 ×

Figure 7—Mixture IV on Cooling Following Cure. 750 ×

been carried out with sulfur as the curing agent. Ostromuislenskii,[8] Stevens,[9] and Fisher and Gray[10] have shown, however, that it is possible to vulcanize rubber with non-sulfur compounds such as *m*-dinitrobenzene and benzoyl peroxide, the physical properties of the cured rubber being similar to those of rubber vulcanized with sulfur.

Experimental

The following experimental work is by no means complete, but was performed in an endeavor to demonstrate the possibilities of micro-vulcanization in the equipment described. Incidentally, it shows the effect of non-sulfur compounds as curing agents.

Five mixtures were cured, mixture I being a control to judge the state of vulcanization of those mixtures cured with non-sulfur agents.

	I	II	III	IV	V
Smoked sheets	100	100	100	100	100
Sulfur	3	..	..	..	..
Litharge	10	10	10	..	..
m-Dinitrobenzene	..	3	3	3	3
Diphenylguanidine	..	..	1	..	1

These mixtures were cured 60, 90, and 120 minutes at 145° C. in a press.

During cure mixture I showed no increase in dispersion of the litharge, the only change observable being a coating of the litharge particles by a layer of lead sulfide, with a consequent darkening of the slide. This conforms with Pohle's[11] assertion that during cure some compounding ingredients cause a chemical reaction which is confined to the surface of the reacting substances. In the case of this compound there is no reappearance after cure of colloidal sulfur and no recrystallization of this element. A further study of this type of mixture would probably throw some light on the fact, known in the rubber footwear and topping industries, that litharge stocks are much less susceptible to bloom than mixtures cured with organic accelerators.

Mixtures II and III were found to cure, but no cure was effected in the case of mixtures IV and V, the criterion of cure being that the vulcanized mixture had nerve, elasticity, and tensile strength of the same order of magnitude as the rubber-sulfur-litharge control mixture.

The photomicrograph (Figure 2) shows mixture II before cure, the *m*-dinitrobenzene being present as light-colored needles, while the dark particles are litharge. When the mixture is heated (Figure 3) the *m*-dinitrobenzene melts at 40° C. and a flow similar to that observed with sulfur cures takes place. No change in the degree of dispersion is discernible.

[8] Ostromuislenskii, *J. Soc. Chem. Ind.*, **35**, 59, 369 (1916).
[9] Stevens, *Ibid.*, **36**, 107 (1917).
[10] Fisher and Gray, IND. ENG. CHEM., **20**, 294 (1928).
[11] Pohle, *Z. wiss. Mikroskop.*, **44**, 183 (1927).

When the mixture cools down after cure (Figure 4) minute colloidal droplets appear, but no recrystallization of the *m*-dinitrobenzene takes place.

Figure 5 shows mixture IV, rubber and *m*-dinitrobenzene, before cure. When this mixture is heated at 145° C. for 2 hours, the *m*-dinitrobenzene melts and an optically empty picture is obtained (Figure 6). No vulcanization takes place, and on cooling an immediate reappearance of *m*-dinitrobenzene crystals is observed (Figure 7).

Mixture V acts in the same manner, no cure taking place and the *m*-dinitrobenzene recrystallizing when the mixture cools.

It would appear that an activator such as a metallic oxide—e. g., litharge—is necessary to secure a cure with *m*-dinitrobenzene, and that diphenylguanidine, a substance which accelerates vulcanization with sulfur, has no appreciable effect with the compound above.

The following two mixtures were cured in order to observe the vulcanization of rubber with benzoyl peroxide:

	VI	VII
Smoked sheets	100	100
Benzoyl peroxide	6⅔	6⅔
Diphenylguanidine	....	1

Each mixture was vulcanized 15 minutes at 130° C., and 15 minutes at 145° C. in a press. A cure was effected according to the criterion set forth above.

Benzoyl peroxide more closely resembled sulfur in that it was capable of vulcanizing rubber without the necessity of an activating agent such as litharge. On heating the benzoyl peroxide melted at 54° C., and upon cooling down after cure it recrystallized in a manner very similar to sulfur recrystallization from a rubber-sulfur mixture. Diphenylguanidine had no effect on cure and no difference was discernible between mixtures VI and VII.

Conclusions

A microscopic study of the course of vulcanization offers many possibilities, especially since, by its aid, the progressive changes which take place during vulcanization can be followed. Using the micropress described above, it is possible to observe these changes and to record the temperature at which they take place.

A rubber-sulfur-litharge mixture after cure exhibits no recrystallization of sulfur even when cured for a very short time. A further microscopical study of the vulcanization of this type of rubber mixture may yield an explanation of the bloom-preventing properties of litharge.

m-Dinitrobenzene and benzoyl peroxide both vulcanize rubber in the absence of sulfur. The former requires an activator such as litharge and does not recrystallize from the mixture when a cure is effected, whereas the latter does not require an activator and recrystallizes after cure in a manner very similar to sulfur.

Acknowledgment

The writer wishes to take this occasion to express his thanks to E. A. Hauser for the interest he has taken in this work and for the helpful suggestions he has given.

[Reprinted from Industrial and Engineering Chemistry,
Vol. 21, No. 4, page 362. April, 1929.]

Chart for the Estimation of Equivalent Cures[1]

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IN ALL heavy rubber articles the temperature conditions which obtain during curing are very different from those existing in light articles. Heat penetrates thin rubber sheets so quickly that they may be said to cure at constant temperature. Heavy articles, however, are heated very slowly, so that their cure may generally be divided into periods of rising temperature, approximately constant temperature, and falling temperature. During August, 1926, the writer developed a method of evaluating and comparing cures made under such variable temperature conditions. The principle is applicable to all cases of variable temperature cures—as, for instance, shoe-curing schedules, etc.

Two papers presenting methods of estimating the curing effect of variable temperature schedules have recently appeared. Sheppard and Wiegand[2] have developed equations and charts whereby curing effect may be calculated and expressed mathematically. Their method is based on the empirical relation that the intensity of curing action doubles with every rise in temperature of A° F., where A is a selected constant (in the example given, 15° F.). The method is therefore limited, in exact application, to compounds for which the temperature interval (A) during which the rate of cure (corresponding to intensity of curing action of the schedule) doubles is actually constant. Tests show that for many stocks the interval is not constant over the range of curing temperatures. The procedure is also limited to schedules where the rate of rise of temperature is constant.

Sherwood[3] has developed a means of predicting the temperature rise during the cure of heavy articles, and both his and Sheppard and Wiegand's papers present graphical methods

[1] Received December 5, 1928.

[2] Sheppard and Wiegand, IND. ENG. CHEM., **20**, 953 (1928).

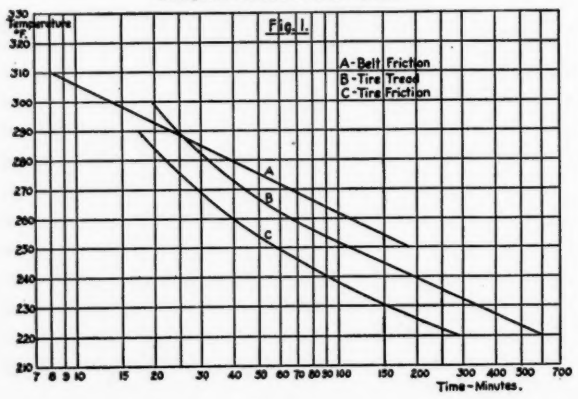
[3] Sherwood, *Ibid.*, **20**, 1181 (1928).

of calculating curing effect which are not subject to the limitations mentioned in the preceding paragraph. The graphical methods have the advantage of presenting curing effect pictorially as well as mathematically. They are open to the objection that, instead of plotting the known quantity, temperature, one must calculate the intensity of curing action corresponding to the temperature, and plot that value.

Principle of Area Diagram

The writer's method of evaluating the curing effect of variable temperature schedules makes use of a chart of special form, termed the "area diagram." A horizontal time scale having uniform graduations is first laid out. Any desired law connecting temperature of curing with time for optimum cure may be selected as the basis of a temperature scale. The vertical temperature scale is then constructed so that the distances of the temperature lines above the base line (time axis) are inversely proportional to the corresponding curing

Comparison of Temperature-Time Relations for Equivalent Cures of Rubber Stocks



times. Then if any lines of time and temperature representing optimum cure are drawn on the chart, the rectangular area enclosed between them and the axes of the diagram will be a constant. Since the vertical distances to the temperature lines are inversely proportional to the corresponding optimum curing times, they are directly proportional to "rate of cure," and the area then represents the product of rate of cure by time, which in any particular case indicates the state of cure of the stock. If referred to the schedule as distinct from the stock to which it is applied, the area may be regarded as the product of intensity of curing action by time, which equals curing effect.

The above statement makes no reference to variable temperature cures, but the principle is easily seen to apply to them, since if any variable temperature schedule is plotted on the chart, the area under the curve may be divided into any

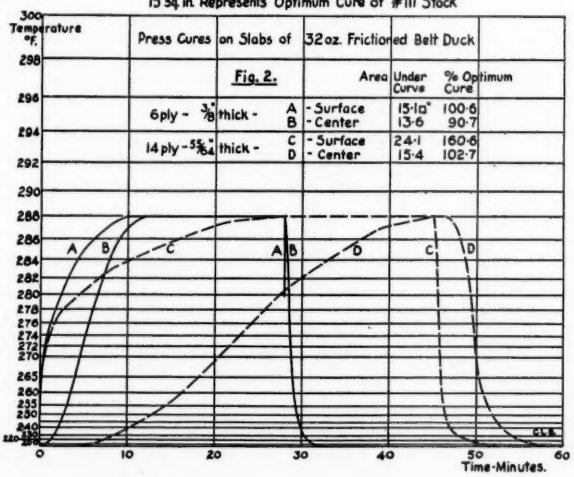
desired number of thin vertical strips, which may be regarded as rectangles. The sum of these small areas represents the curing effect of the schedule. In use, then, the temperature schedule under consideration is plotted on the area diagram. The resulting curve presents, graphically, the curing effect of the schedule, or the state of cure of the stock subjected to that schedule, and the area under the curve, which may best be determined by the planimeter, gives a mathematical expression of these properties. Since the known area representing optimum cure is a constant, if the curve encloses this area the stock is in the state of optimum cure. If the area is less than that for optimum cure, the stock is undercured, and if more, overcured.

Applications

Three examples of actual construction and use of the area diagram are given below:

AREA DIAGRAM #4 - INTERVAL 13½°.
15 sq. in. Represents Optimum Cure of #111 Stock

Press Cures	on Slabs of	32 oz. Frictioned Belt Duck		
	Fig. 2.		Area Under Curve	% Optimum Cure
6 ply - 3/8" thick -	A - Surface		15·10°	100·6
	B - Center		13·6	90·7
14 ply - 55/64" thick -	C - Surface		24·1	160·6
	D - Center		15·4	102·7



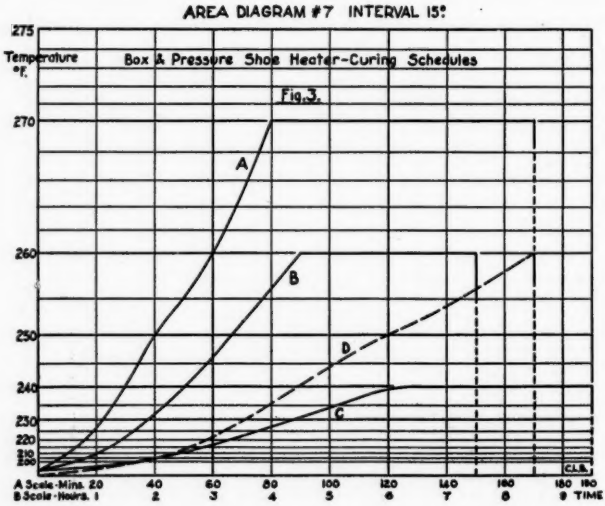
(1) The original chart was derived from experimental press cures on a high-grade belt friction, resilient energy and tensile product being used as cure criteria. It was found that the time for optimum cure was halved, or the rate of cure doubled, for every increase in temperature of 13.5° F. The curve showing optimum cure of thin molded sheets, *A*, Figure 1, is a straight line on semi-logarithmic paper, having the approximate equation $T = 350.15 - 44.15 \log t$, where T is temperature in degrees Fahrenheit, and t is time in minutes.

The area diagram of Figure 2 is drawn from this formula. The time scale is 1.5 inches = 10 minutes. From the equation the time for optimum cure at 300° F. is found to be 13.674 minutes. This is represented on the time scale by a length of $\frac{13.674}{10} \times 1.5 = 2.0511$ inches. An area of 15 square inches was selected to represent optimum cure. Then, by definition, the 300° F. temperature line must be $\frac{15}{2.0511} = 7.313$ inches above

the base line. The distance up for any other temperature line is found by simple proportion. For example, when $T = 290$, $t = 23.04$, and the 290° F. line is $\frac{13.674}{23.04} \times 7.313 = 4.34$ inches above the base line. Now a time of 23.04 minutes is represented on the time scale by $\frac{23.04}{10} \times 1.5 = 3.46$ inches and $3.46 \times 4.34 = 15.02$ (approx. 15) square inches.

On the chart are shown temperatures taken by means of thermocouples built into the material, during the cure of two slabs of frictioned belt duck. The areas developed by the different curves indicate the over- and under-cures of the stocks at different points in the slabs. The amounts of the over- and under-cures are indicated by expressing the different areas as percentages of the area which represents optimum cure.

(2) Temperature-time curves showing optimum cure on thin molded sheets of high-grade tire tread and friction stocks are shown on Figure 1 by curves *B* and *C*, respectively. In these cases the temperature interval during which rate of cure doubles



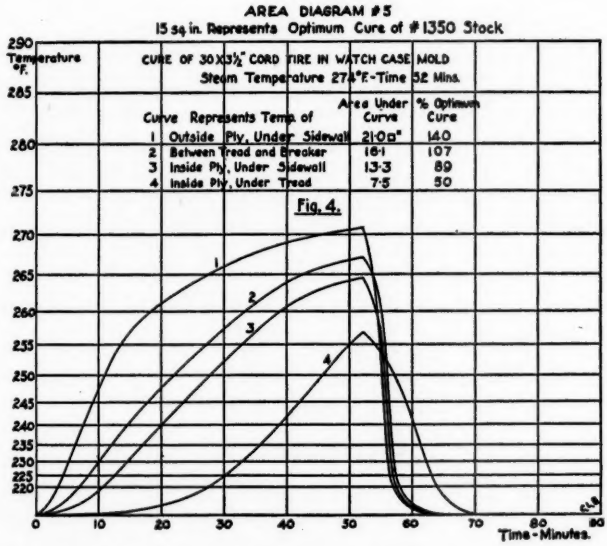
is not constant over the curing range. No simple equation was found for these curves. To obtain the area diagram of Figure 4, curve *C* was drawn to an open scale and corresponding values of temperature and time were read off. After selecting the time scale and a suitable area (15 square inches) to represent optimum cure, the temperature scale was arranged by proportion as before.

On Figure 4 are plotted the results of a thermocouple test on a tire cured in a watchcase heater. Since the chart is applied to the stock from which it was developed, an accurate indication of the state of cure of the friction stock in different parts of the tire is obtained.

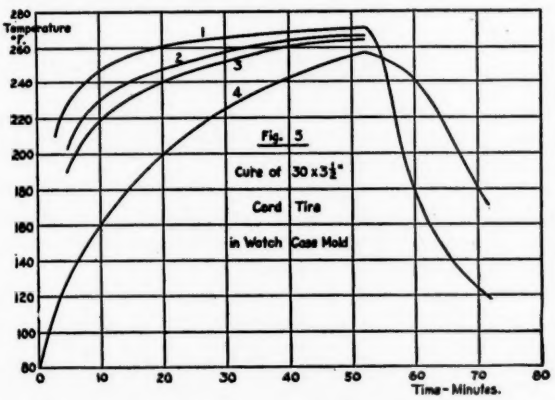
Comparison of Figures 4 and 5 illustrates the value of the area diagram in presenting the curing effect under conditions of variable temperature. The temperature scale of Figure 5 has uniform graduations. The form of the curves in Figure 5 and the areas under them are entirely misleading as far as the state of cure of the stock in different parts of the tire is concerned.

(3) Figure 3 shows an area diagram with the temperature scale designed to fit the case where rate of cure is assumed to

double for every rise in temperature of 15° F. In this case the distance of any temperature line above the datum is a constant factor $(1/X)$ of the distance, for the next, 1-degree, higher line, and $X^{15} = 2$ or $X = 1.0473$. The 270° F. line is 6.0 inches above the base. Then the 269° F. line is $\frac{1}{1.0473}$ of 6.0 or 5.730 inches,



and the 268° F. line is $\frac{1}{1.0473}$ of 5.730, or 5.471 inches, above the datum, and so on. Such a continuous calculation is extremely accurate when done by logarithms. A check on the results is provided by such obvious values as the distance for the 255° F. line which is one-half of 6.0 or 3.0 inches, and for the 240° F. line which is one-half of 3.0 or 1.5 inches, etc.



No definite area for optimum cure is assigned to this diagram, since it is intended as a general chart to be used in comparing similar cures on an approximate basis only. In

Figure 3 are shown some shoe-curing schedules whose characteristics are summarized in Table I.

Table I

Curve	Schedule	Total Time	Max. Temp.	Drawn to Scale	Areas	
		Minutes	° *F.*		*A* scale	*B* scale
	Pressure cure:					
A	For boots	170	270	*A*	36.8	
B	For tennis	150	260	*A*	18.0	
C	For crepe	190	240	*A*	8.9	
D	Box-heater for boots	8½ hours	260	*B*		12.9 = 38.7 on *A* scale

Since the stocks which would be cured in the different heats are generally of different types and would follow very different laws of equivalent cures, the areas shown in the table must be regarded as referring only to curing effect as a property of the schedule and not to the state of cure which would be produced in any particular stock (see paragraphs 3 and 4 in the summary). The greatest value of the area diagram in this connection is the accurate means it provides of making relatively small changes in the characteristics of any one schedule, while still retaining the original curing effect, or for the purpose of changing the curing effect by a desired amount.

Summary of Characteristics of Area Diagram

1—The diagram provides an accurate means of evaluating the curing effect of any given variable temperature schedule no matter how irregular. The process is reversible; i. e., when a schedule having a certain curing effect is desired, it is merely necessary to construct one with the proper area, having regard, of course, to proper heating and cooling periods.

2—The results are presented both graphically and mathematically.

3—Where absolute accuracy is desired, the chart may be drawn in accordance with the equivalent cure relation of the stock for which it is to be used, whether that relation is of simple exponential form or not. (The danger of applying any one equivalent cure relation to a great variety of stocks is shown by the three curves of Figure 1. Widely different results will be obtained if the equivalent of any one given cure is calculated by the three relations.)

4—If only approximate results are desired, a series of diagrams can be drawn, based on different equivalent-cure relations, and cures for any stock can be calculated by means of the diagram most suited to it.

5—The same chart may be accurately applied to any number of stocks having the same form of equivalent cure relation, whether the individual stocks are quick or slow curing, it being merely necessary to find the area representing optimum cure of each stock.

6—The charts can be cheaply reproduced from tracing paper drawings by any dry printing process which does not distort the printing paper.

Acknowledgment

Acknowledgment is due Gutta Percha & Rubber, Limited, for permission to publish this article.